

# JILANI MANUAL OF PRACTICAL CHEMISTRY

FOR B.Sc. / B.S. & M.Sc

Vol. II (Inorganic Chemistry)

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**Jilani Notes**

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# *Instruction for the Laboratory work*

## **Laboratory Manners**

Laboratory is a place where knowledge gained in the class room is confirmed by practical work. Keep in mind the following points when you come to the laboratory to perform experiments:

1. Read all details about the practical you are going to perform from your notebook. Always come to the laboratory well prepared.
2. Put on your lab coat during practical to save your clothes.
3. Supply of water should be checked, doors and windows should be opened and exhaust fan should be turned on before starting practical work.
4. Clean your working table before starting experiment.
5. Wash the glass apparatus before use and handle it carefully. Any breakage should be reported to the class teacher.
6. Broken glass pieces, waste papers, match sticks, used filter papers and litmus papers should be thrown into waste box.
7. Bring your practical notebook, platinum wire, fractional weights, pencil, sharpener, eraser, and the ruler with you when you come to laboratory to do practical.
8. Work quietly and systematically in the laboratory.
9. Do not waste water, gas, or chemicals in the laboratory. Be economical in the use of chemicals. Never bring reagent bottles from side shelves to your table.
10. Do not taste any chemical in the laboratory without the advice of your teacher.
11. Do not take food and drink in the laboratory.
12. Do not interchange the corks of the reagent bottles.
13. Never mix the chemicals unnecessarily.
14. Lightened matchsticks should not be thrown on the table, on the floor or in the waste box.
15. Wash your hands with soap before leaving the laboratory.
16. Record your observations in your practical Note-Book and get it signed by the teacher before leaving laboratory.

## **Safety Precautions**

Always observe the following precautions during practical.

1. Follow the Hazard Symbols printed on the reagent bottles which guide or warn you about the possible danger. Hazard symbols printed on the reagent bottles are given in the table I.1.
2. Never heat glass apparatus (beakers, flask) directly on flame. Always use wire gauze for heating glass apparatus.
3. Never mix chemicals simply for nothing. Mixing of chemicals without any purpose may cause a serious accident.
4. Reagent once taken from the reagent bottles should not be poured back into the bottles.
5. Never pour water into concentrated acid rather acid should be poured into water.
6. Never bring the inflammable liquids (ether, alcohol, acetone, kerosene, oil, and petrol) near the naked flame.
7. Never smell the gases excessively.
8. Do not perform unauthorized experiments.



# Qualitative Inorganic Analysis

## 2.1. Basic terminology

**Qualitative analysis of salt:** Qualitative analysis is the study of composition of a substance. Detection of the radicals in a salt by dry and wet tests is called qualitative analysis. Different techniques are used for Qualitative analysis.

**Macro analysis:** Amount of sample used in this type of analysis is 1-10 g.

**Semi-micro analysis:** Amount of sample used in this type of analysis is 10-100 mg.

**Micro analysis:** Amount of sample used in this type of analysis is 1-10 mg.

**Ultra-micro analysis:** Amount of sample used in this type of analysis is less than 1 mg.

**Salt:** A compound formed by neutralization of acid by a base (other than water) is called a salt e.g. NaCl is a salt formed by neutralization of NaOH with HCl.



**Radical:** An atom or group of atoms which retains its identity (does not decompose) in a chemical reaction is called a radical.

**Types of Radicals:** Radicals are of two types:

**Basic Radical:** A radical carrying positive charge is called a basic radical, e.g.,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  etc.

**Acid Radicals:** A radical carrying negative charge is called an acid radical, e.g.,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc.

## Systematic Qualitative Analysis of Inorganic Substances

An inorganic compound consists of an acid and a basic radical. Purpose of the qualitative analysis of inorganic substances is the detection and identification of cations and anions in the given mixture or salt.

## 2.2 Classification of basic radicals

Basic radicals are divided into six groups depending on the insolubility of their precipitate

Group-I	:	$\text{Ag}^+$ , $\text{Pb}^{2+}$ , $\text{Hg}_2^{2+}$
Group-II	:	$\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Bi}^{3+}$ , $\text{As}^{3+}$ , $\text{Sn}^{2+}$ , $\text{Sb}^{3+}$ , $\text{Sn}^{4+}$
Group-III	:	$\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$
Group-IV	:	$\text{Zn}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$
Group-V	:	$\text{Ca}^{2+}$ , $\text{Ba}^{2+}$ , $\text{Sr}^{2+}$
Group-VI	:	$\text{NH}_4^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$



## Classification of acid radicals

There is no well defined classification of the acids radicals. However depending on their tendency to react with dilute or concentrated acids or with a particular reagent, the acid radicals may be divided into following groups for preliminary information about the acid radicals in the mixture.

**Group I (The volatile Group):** The anions (acid radicals) of this group react with dilute and nonoxidizing acids to produce volatile products. The anions included in this group are:  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{S}^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{ClO}^-$ . These radicals react with dil. acids like  $\text{H}_2\text{SO}_4$  and produce characteristic gases, that is why, this group is called volatile group.












## COLOURS AND APPEARANCE OF SOME SALTS

Colours of the solid salts	Inference/ Remarks
 <b>Colourless</b>	Group I, II, III metal salts; no transition metal ions present. Ammonium compounds e.g. $\text{NH}_4\text{Cl}$ , $\text{NH}_4\text{NO}_3$
 <b>Blue crystals</b>	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (hydrated) as shown. $\text{Cu}(\text{NO}_3)_2$
 <b>Green crystals</b>	$\text{CuCl}_2$
 <b>Pale green crystals</b>	Hydrated iron(II) salts e.g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
 <b>Brown crystals</b>	Fe(III) salts e.g. hydrated $\text{FeCl}_3$
 <b>Orange crystals</b>	$\text{K}_2\text{Cr}_2\text{O}_7$
 <b>Purple crystals</b>	$\text{KMnO}_4$ (purple lustre)
 <b>Black crystals</b>	Iodine crystals
 <b>White powder</b>	$\text{CaCO}_3$ , $\text{ZnCO}_3$ , $\text{ZnO}$ (when cold); Anhydrous $\text{CuSO}_4$
 <b>Yellow powder</b>	Lead(II) oxide, $\text{PbO}$ as shown. $\text{ZnO}$ (yellow when hot and white when cold), $\text{AgI}$ (pale yellow ppt), $\text{PbI}_2$ (bright yellow ppt).
 <b>Bright orange powder</b>	Dilead(II) lead(IV) oxide, $\text{Pb}_3\text{O}_4$
 <b>Green powder</b>	$\text{CuCO}_3$
 <b>Reddish brown solid or powder</b>	$\text{Cu}_2\text{O}$ , copper(I) oxide (reddish brown) as shown. Iron(III) oxide, $\text{Fe}_2\text{O}_3$ , $\text{Fe}(\text{OH})_3$ , $\text{PbO}_2$ (dark brown)
 <b>Black powder</b>	$\text{CuO}$ , $\text{FeO}$ , $\text{MnO}_2$ , carbon powder



## COLOURS OF SOLUTIONS OF SOME SALTS

Colours of solution	Inference/ Remarks
 <b>Colourless</b>	Group I, II & III cations; most acids and alkalis; hydrogen peroxide, limewater
 <b>Blue</b>	$\text{Cu}^{2+}$ ions in solution
 <b>Pale green</b>	$\text{Fe}^{2+}$ ions in solution (pale green), $\text{Cr}^{3+}$ , Ni
 <b>Green</b>	$\text{Cr}^{3+}$ , $\text{Ni}^{2+}$ , $\text{CuCl}_2$ solution
 <b>Yellow/yellow brown</b>	$\text{Fe}^{3+}$ ions in solution, $\text{K}_2\text{CrO}_4$
 <b>Dark blue</b>	Complex ion of $\text{Cu}^{2+}$ : $\text{Cu}(\text{NH}_3)_4^{2+}$
 <b>Purple</b>	$\text{KMnO}_4$ (potassium permanganate)
 <b>Effervescence</b>	$\text{CO}_3^{2-}$ or $\text{HCO}_3^{-}$
 <b>Pale yellow ppt.</b>	Confirmatory test of $\text{I}^-$ $\text{Ag}^+ (\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{AgI} (\text{s})$



**Group II (The Barium chloride Group):** The anions of this group react with  $\text{BaCl}_2$  to yield insoluble compounds. This group may be further divided into sub groups.

**Group II-A:** Precipitate formed with  $\text{BaCl}_2$  is insoluble in acetic acid:  $\text{SO}_4^{2-}$  and  $\text{C}_2\text{O}_4^{2-}$

**Group II-B:** Precipitate formed with  $\text{BaCl}_2$  is soluble in acetic acid:  $\text{PO}_4^{3-}$ ,  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ,  $\text{BO}_3^{3-}$

**Group III (The Silver nitrate Group):** The anions react with silver nitrate and form products which are insoluble in dil. nitric acid. This group include  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$  and  $[\text{Fe}(\text{CN})_6]^{4-}$ .

**Group IV (The Soluble Group):** These anions do not form volatile products with dil. acids and their silver and barium salts are soluble. These anions include  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{MnO}_4^-$  and  $\text{ClO}_3^-$ .

## Scheme of Analysis of Acid Radicals

### Group I (The volatile Group):

#### Procedure:

Take about 0.5 g of solid salt in a dry test tube and add 2-3 mL dil.  $\text{H}_2\text{SO}_4$  and observe any change. If reaction occurs, then anions of the Group I (Volatile Group) are indicated ( $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$ ). Warm the test tube if necessary. Observe and identify the volatile products as given in the table.

Note: Never boil the salt with dil. acid.

When a salt reacts with dil.  $\text{H}_2\text{SO}_4$ , A gas characteristic of the radicals evolves which indicates the presence of acid radical. Note the odour, colour or ability of the gas to react with a particular reagent.

**CAUTION!** Sulphuric acid is a strong acid. It must be handled carefully. It cause burns and if ingested, permanent damage may occur. Inhalation is very dangerous and fatal. Never pour water into acid to dilute acid rather put acid into water to make dilute solution. In case of contact with skin or any body part, wash the effected part with dilute sodium carbonate solution first and then with plenty of water. Consult the doctor in case of any accident.

### Identification of radicals of Group I

Observations	Inferences
<p>1. A colourless, odourless gas evolves with effervescence (rapidly) which turns lime water milky. This gas is carbon dioxide.</p> $\text{CO}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ <p>Distinction between <math>\text{CO}_3^{2-}</math> or <math>\text{HCO}_3^-</math></p> <p>Dissolve about a small quantity of solid mixture in water and filter. To filtrate add solution of <math>\text{MgSO}_4</math>.</p> <p>White ppt. in cold</p> <p>White ppt. on heating the test tube</p> <p>2. A colourless gas comes out which turns lead acetate paper black.</p> <p>Procedure: Dip a piece of filter paper in lead acetate solution and place it over the mouth of the test tube. Paper becomes black. The gas is <math>\text{H}_2\text{S}</math>.</p> $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{S} \longrightarrow \text{PbS}_{(\text{black})} + \text{CH}_3\text{COOH}$	<p><math>\text{CO}_3^{2-}</math> or <math>\text{HCO}_3^-</math> indicated.</p> <p><math>\text{CO}_3^{2-}</math> indicated</p> <p><math>\text{HCO}_3^-</math> indicated</p> <p><math>\text{S}^{2-}</math> indicated.</p>
<p>3. A colourless gas with suffocating odour like burning of sulphur or match stick which turns the acidified potassium dichromate paper green. The gas is <math>\text{SO}_2</math> which comes from sulphites.</p> <p>Procedure: Dip a piece of filter paper in potassium dichromate solution and then in dil <math>\text{H}_2\text{SO}_4</math>. Hold this paper over the mouth of test tube. Paper becomes green.</p>	<p><math>\text{SO}_3^{2-}</math> indicated.</p>
<p>4. A colourless gas with suffocating odour like burning sulphur or match stick which turns the acidified potassium dichromate paper green and contents of the test tube become yellow due to liberation of free sulphur from thiosulphate.</p> <p>Procedure: Dip a piece of filter paper in a solution of potassium dichromate and then in a solution of dil <math>\text{H}_2\text{SO}_4</math>. Hold this paper over the mouth of the test tube. Paper becomes green.</p>	<p><math>\text{S}_2\text{O}_3^{2-}</math> indicated.</p>
<p>5. Reddish brown gas evolves with pungent odour which turns ferrous sulphate paper black. The gas is <math>\text{NO}_2</math> which comes from nitrites.</p>	<p><math>\text{NO}_2^-</math> indicated.</p>



### Test for $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$ :

$\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  are analyzed as given in the table below.

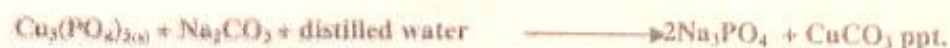
Experiments	Observations	Inferences
<b>Carbonate (<math>\text{CO}_3^{2-}</math>)</b> Dissolve about 100 mg of the solid mixture in water and filter. The filtrate is called aq. solution (i) Aq. Solution + $\text{Mg SO}_4$ solution (ii) O.S + $\text{CaCl}_2$ solution	White ppt. in cold state. White ppt. in cold state	$\text{CO}_3^{2-}$ confirmed $\text{CO}_3^{2-}$ confirmed
<b>Carbonate [<math>\text{CO}_3^{2-}</math> insoluble]</b> Solid Salt + $\text{H}_2\text{O}$	Solid remains insoluble.	Insoluble $\text{CO}_3^{2-}$ such as carbonates of $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ba}^{2+}$ and $\text{Sr}^{2+}$ confirmed.
<b>Bicarbonate (<math>\text{HCO}_3^-</math>)</b> (i) Aq. Solution + $\text{Mg SO}_4$ solution (ii) Aq. solution. + $\text{CaCl}_2$ solution	White ppt. on heating White ppt. on heating.	$\text{HCO}_3^-$ confirmed. $\text{HCO}_3^-$ confirmed

### Tests for $\text{SO}_3^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{NO}_2^-$ , $\text{S}^{2-}$

These radicals are confirmed by wet tests performed with the solution of salts.

#### Preparation of solution for analysis of acid radicals

- Dissolve small quantity of salt in cold or hot distilled water. If homogeneous transparent solution is formed, it is called aqueous solution or original solution.
- If salt does not dissolve in water, take about 1 g salt and 4 g  $\text{Na}_2\text{CO}_3$  in a beaker containing about 50 mL distilled water. Boil the mixture until the evolution of gas stops. Filter the solution and discard residue. Add  $\text{CH}_3\text{COOH}$  to filtrate until effervescence stops. Heat the solution again to expel  $\text{CO}_2$  gas. Allow to cool and then add ammonia solution until just alkaline. Boil again for 1 minute to expel  $\text{NH}_3$ . Perform wet test with this solution. This solution is called  $\text{Na}_2\text{CO}_3$  - extract. It cannot be used for the confirmation of  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CH}_3\text{COO}^-$ .



### Test for Sulphide $\text{S}^{2-}$

Experiments	Observations	Inferences
<b>Sulphide (<math>\text{S}^{2-}</math>)</b> $\text{Na}_2\text{CO}_3$ - extract + Sodium nitroprusside solution $\text{Na}_2\text{CO}_3$ - extract + $\text{Pb}(\text{CH}_3\text{COO})_2$ solution	Violet colour, Black ppt.	$\text{S}^{2-}$ confirmed. $\text{S}^{2-}$ confirmed.

### Test for $\text{SO}_3^{2-}$ , $\text{S}_2\text{O}_3^{2-}$ , $\text{NO}_2^-$

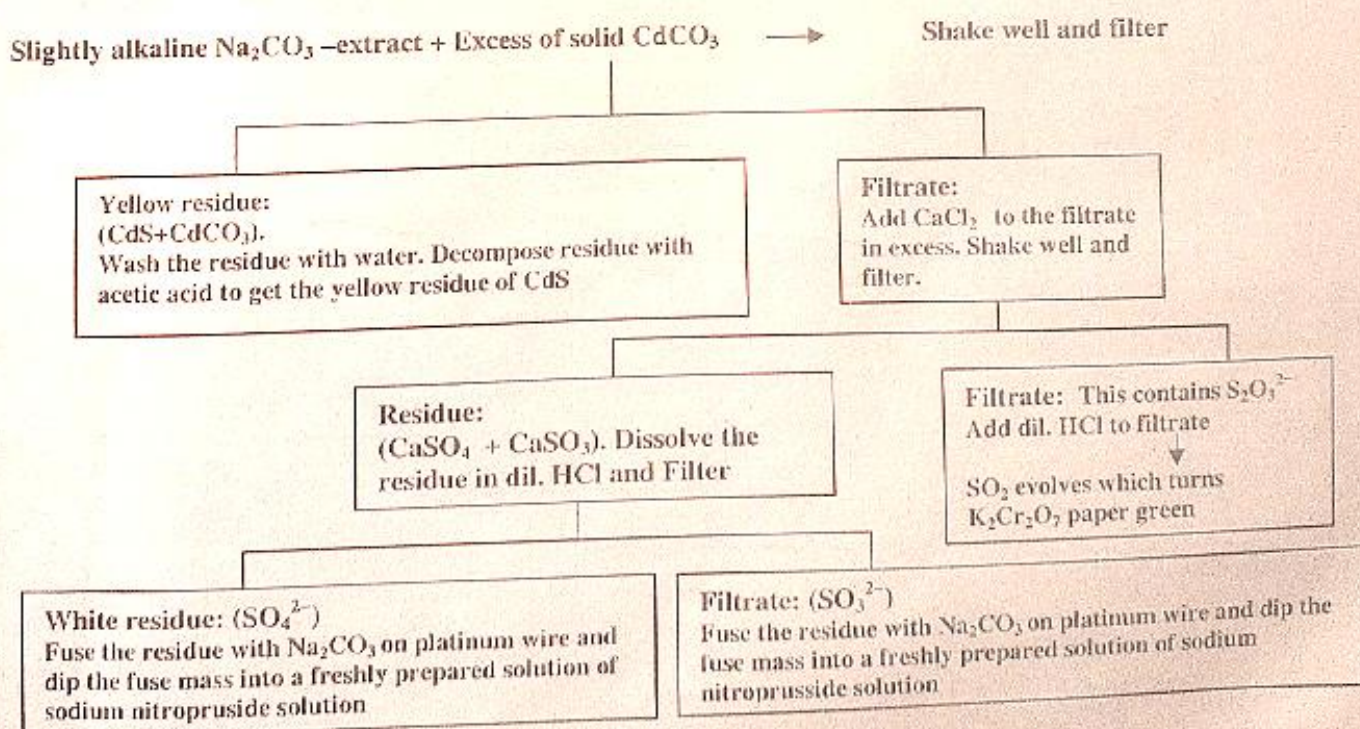
If Sulphide ( $\text{S}^{2-}$ ) is present, add  $\text{Pb}(\text{CH}_3\text{COO})_2$  solution to 10 mL of  $\text{Na}_2\text{CO}_3$  - extract till complete precipitation and filter. Discard the black ppt. of  $\text{PbS}$  and divide the filtrate into three portions and perform tests for  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{NO}_2^-$  as given in the table.



Table: Test for  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{NO}_2^-$

Discard Black residue of PbS	Filtrate	Portion II of $\text{Na}_2\text{CO}_3$ - extract Sulphite	Portion III of $\text{Na}_2\text{CO}_3$ - extract Thiosulphate
	Portion I of $\text{Na}_2\text{CO}_3$ - extract Nitrite		
	<p>Filtrate + <math>\text{CH}_3\text{COOH}</math> + <math>\text{FeSO}_4</math> solution <math>\rightarrow</math> Dark brown colouration. Nitrite indicated.</p> <p><u>Confirmatory Tests</u></p> <p>Filtrate + <math>\text{NH}_4\text{Cl}</math> <math>\xrightarrow{\text{Heat}}</math> Nitrogen evolved with effervescence. <math>\text{NO}_2^-</math> confirmed</p> <p>Filtrate + <math>\text{NH}_4\text{Cl}</math> + solid <math>\text{CoCl}_2</math> + acetic acid <math>\xrightarrow{\text{warm}}</math> yellow ppt. <math>\text{NO}_2^-</math> confirmed</p> <p>Place 2-3 drops of <math>\text{Na}_2\text{CO}_3</math> - extract on spot plate and add a crystal of <math>\text{FeSO}_4</math> and 2-3 drops of acetic acid <math>\rightarrow</math> Brown colour of <math>[\text{Fe}(\text{NO})]^{2+}</math> <math>\text{NO}_2^-</math> confirmed</p> <p>Treat 20-30 mg mixture with 1mL of acetic acid and 3 drops of solution of <math>\text{FeCl}_3</math> <math>\rightarrow</math> Red colouration. Nitrite confirmed</p> <p><math>\text{NO}_2^-</math></p>	<p>Filtrate + <math>\text{BaCl}_2</math> sol. <math>\rightarrow</math> White ppt. soluble in dil. <math>\text{HCl}</math></p> <p>Sulphite indicated</p> <p><u>Confirmatory Tests</u></p> <p>Filtrate + Iodine <math>\rightarrow</math> colour discharge. Sulphite confirmed</p> <p>Filtrate + dil. <math>\text{H}_2\text{SO}_4</math> + <math>\text{K}_2\text{Cr}_2\text{O}_7</math> sol. <math>\rightarrow</math> Orange colour changes to green. Sulphite confirmed</p> <p><math>\text{Na}_2\text{CO}_3</math> - extract + <math>\text{Pb}(\text{CH}_3\text{COO})_2</math> sol. <math>\rightarrow</math> White ppt. Sulphite confirmed</p> <p>2-3 drops <math>\text{Na}_2\text{CO}_3</math> - extract + few drops of hot saturated solution of <math>\text{Hg}_2\text{Cl}_2</math> <math>\rightarrow</math> White ppt. Sulphite confirmed</p> <p><math>\text{SO}_3^{2-}</math></p>	<p>Filtrate + <math>\text{CH}_3\text{COOH}</math> + <math>\text{AgNO}_3</math> Sol. <math>\rightarrow</math> White ppt. which changes to brown and finally black. Thiosulphate indicated</p> <p><u>Confirmatory Tests</u></p> <p>Filtrate + <math>\text{FeCl}_3</math> sol. <math>\rightarrow</math> Purple colour. Thiosulphate confirmed</p> <p>Filtrate + dil. <math>\text{HCl}</math> <math>\rightarrow</math> Solution becomes turbid due to free sulphur. A gas comes which turns <math>\text{K}_2\text{Cr}_2\text{O}_7</math> paper green. Thiosulphate confirmed</p> <p>2-3 drops of neutral <math>\text{Na}_2\text{CO}_3</math> - extract + A drop of iodine reagent <math>\rightarrow</math> Colour of iodine discharged. Thiosulphate confirmed.</p> <p><math>\text{S}_2\text{O}_3^{2-}</math></p>

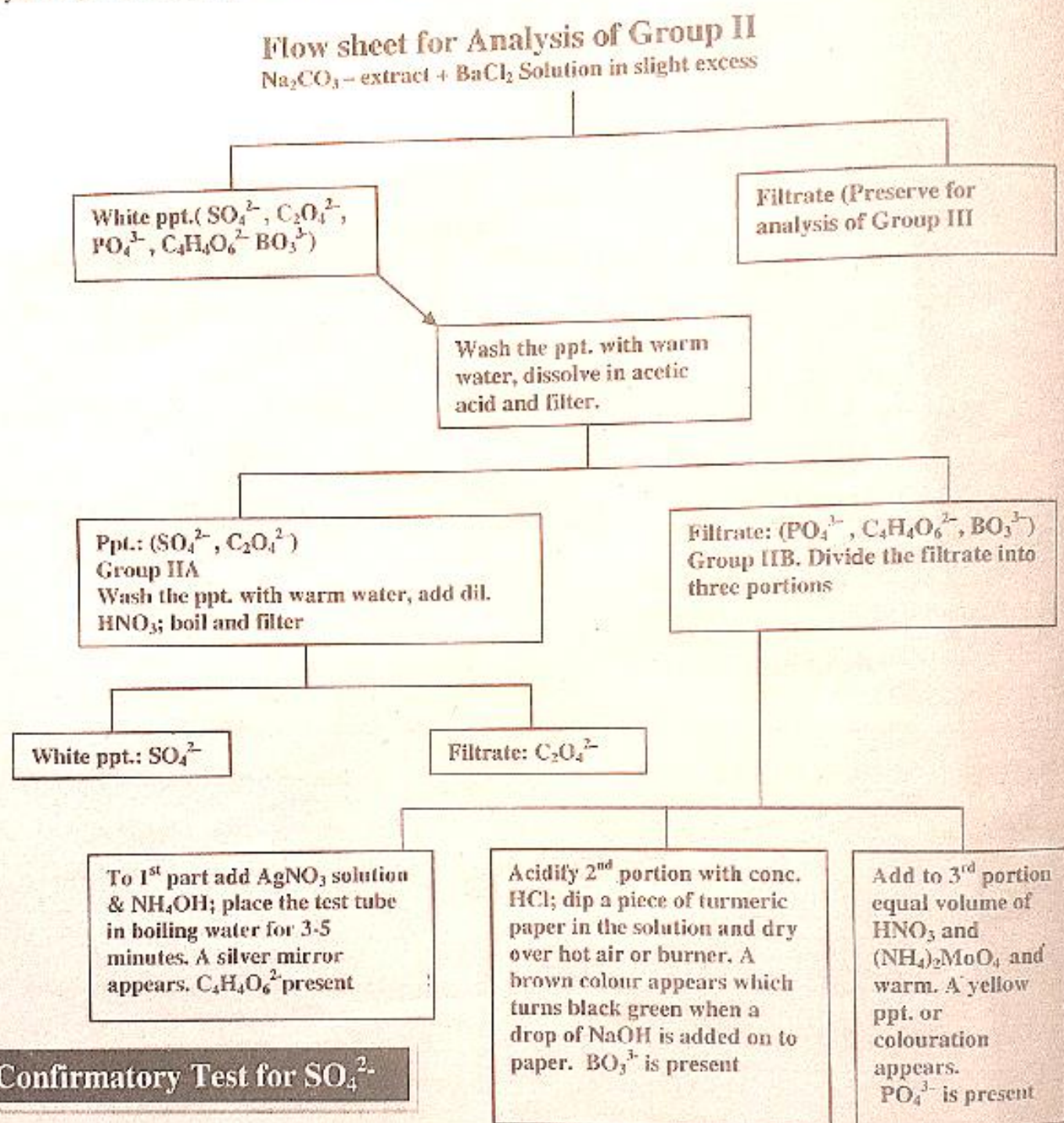
Flow Sheet for Analysis of  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$  in presence of each other





**Group II (The Barium chloride Group):**  $\text{SO}_4^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{C}_4\text{H}_4\text{O}_6^{2-}$ ,  $\text{BO}_3^{3-}$

Analyze the group according to the following flow diagram.



### Confirmatory Test for $\text{SO}_4^{2-}$

No	Experiments	Observations	Inference
1	Mix the ppt. with equal quantity of $\text{Na}_2\text{CO}_3$ and charcoal powder and fuse the mass on a match stick or iron wire loop. Extract the fuse mass with hot water and filter. Add 2-3 drops of sodium nitroprusside to 2-3 drops of filtrate	A violet colour due to $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$	$\text{SO}_4^{2-}$ confirmed
2	$\text{Na}_2\text{CO}_3$ -extract + dil. $\text{HCl}$ + $\text{BaCl}_2$ solution	White ppt.	$\text{SO}_4^{2-}$ confirmed



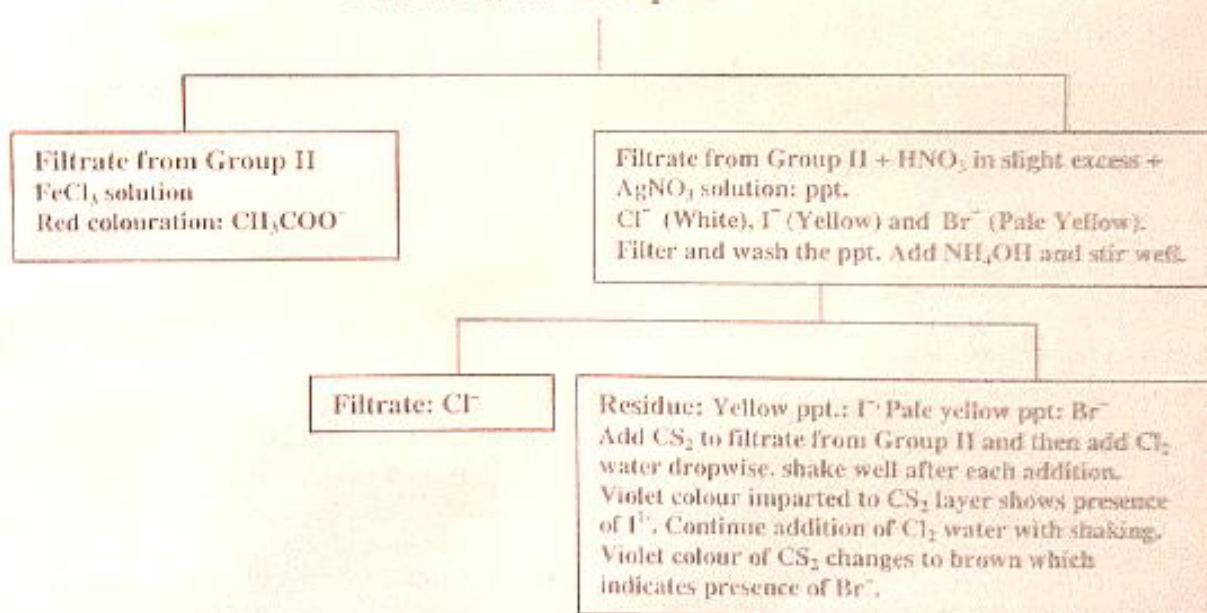
### Confirmatory Tests for $C_2O_4^{2-}$

No	Experiments	Observations	Inference
1	$Na_2CO_3$ - extract + $BaCl_2$ Solution in slight excess and filter. Filtrate + dil. $H_2SO_4$ + $KMnO_4$ dropwise	$KMnO_4$ decolourized	$C_2O_4^{2-}$ confirmed
2	Filtrate from above + A crystal of resorcinol + Con. $H_2SO_4$	Blue ring at the junction of three liquids	$C_2O_4^{2-}$ confirmed

### Confirmatory Tests for $C_4H_4O_6^{2-}$ , $PO_4^{3-}$ , $BO_3^{3-}$

No	Experiments	Observations	Inference
1	$Na_2CO_3$ - extract + $BaCl_2$ Solution in slight excess and filter. Ppt + acetic acid + Few drops $CuSO_4$ solution	Bright blue solution	$C_4H_4O_6^{2-}$ confirmed
2	Solid mixture + Conc. $H_2SO_4$ + Ethanol $\longrightarrow$ stir with glass rod and ignite the vapors	Green edged flame	$BO_3^{3-}$ confirmed
3	Neutral $Na_2CO_3$ - extract + $CoCl_2$ solution	Violet blue colour	$PO_4^{3-}$ confirmed
4	Neutral $Na_2CO_3$ - extract + Few drops $HNO_3$ + $AgNO_3$	Yellow ppt	$PO_4^{3-}$ confirmed

### Group III (The Silver nitrate Group): $Cl^-$ , $Br^-$ , $I^-$ , and $CH_3COO^-$ Filtrate from Group II





## Confirmatory Tests for $\text{CH}_3\text{COO}^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , and $\text{I}^-$

No	Experiments	Observations	Inference
1	Solid mixture + Conc. $\text{H}_2\text{SO}_4$ + Ethanol $\xrightarrow{\text{Heat}}$	A fruity smell, more pronounced on cooling and dilution	$\text{CH}_3\text{COO}^-$ confirmed
2	Neutral $\text{Na}_2\text{CO}_3$ -extract + $\text{FeCl}_3$	Red colouration	$\text{CH}_3\text{COO}^-$ confirmed
3	$\text{Na}_2\text{CO}_3$ -extract + dil $\text{HNO}_3$ + $\text{AgNO}_3$	White ppt soluble in $\text{NH}_4\text{OH}$	$\text{Cl}^-$ confirmed
4	Chromyl chloride test: Solid mixture + $\text{K}_2\text{Cr}_2\text{O}_7$ + Conc. $\text{H}_2\text{SO}_4$ $\xrightarrow{\text{Heat}}$ pass the vapours ( $\text{CrO}_2\text{Cl}_2$ ) in a test tube containing $\text{NaOH}$ solution; acidify with acetic acid + $\text{Pb}(\text{CH}_3\text{COO})_2$ solution dropwise	A thick yellow ppt. is formed	$\text{Cl}^-$ confirmed
4	$\text{Na}_2\text{CO}_3$ -extract + dil $\text{HNO}_3$ + $\text{AgNO}_3$ solution	A pale yellow ppt. partially soluble in $\text{NH}_4\text{OH}$	$\text{Br}^-$ confirmed
5	Solid mixture + $\text{MnO}_2$ + Conc. $\text{H}_2\text{SO}_4$ $\xrightarrow{\text{Heat}}$	Reddish brown vapours of bromine which bleaches the litmus paper.	$\text{Br}^-$ confirmed
6	$\text{Na}_2\text{CO}_3$ -extract + dil $\text{HNO}_3$ + $\text{AgNO}_3$ solution	A yellow ppt. insoluble in $\text{NH}_4\text{OH}$	$\text{I}^-$ confirmed
7	Mix one drop of neutral sodium extract with one drop of starch solution on a spot plate and add a drop of $\text{KNO}_2$ solution (acidify) if necessary.	A blue colour develops	$\text{I}^-$ confirmed

**Group IV (The Soluble Group):** These anions do not form volatile products with dil. Acids and their silver and barium salts are soluble. These anions include  $\text{NO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{MnO}_4^-$  and  $\text{ClO}_3^-$ . These ions are individually.

### Tests for $\text{NO}_3^-$

No	Experiments	Observations	Inferences
1.	Add few drops of diphenylamine to few drops of $\text{Na}_2\text{CO}_3$ - extract along the wall of test tube	A dark blue colour at the junction of two solutions.	$\text{NO}_3^-$ confirmed
2.	To few drops of acidified $\text{Na}_2\text{CO}_3$ - extract, few drops of $\text{FeSO}_4$ was added and Conc. $\text{H}_2\text{SO}_4$ was added to this solution along the walls of the test tube.	A brown ring was formed at the junction of the conc. Conc. $\text{H}_2\text{SO}_4$ and $\text{FeSO}_4$	$\text{NO}_3^-$ confirmed
3.	To 1 mL neutral $\text{Na}_2\text{CO}_3$ - extract, add 0.5 g $\text{Al/Zn}$ or Devarda's alloy and boil	A gas with ammonia smell evolved which turns $\text{HgNO}_3$ paper black	$\text{NO}_3^-$ confirmed



Tests for  $\text{CH}_3\text{COO}^-$ 

N	Experiments	Observations	Inferences
0			
1	Solid mixture + conc. $\text{H}_2\text{SO}_4$ + Ethanol $\xrightarrow{\text{Heat}}$	A fruity smell, more pronounced on cooling and dilution	$\text{CH}_3\text{COO}^-$ confirmed
2	Neutral $\text{Na}_2\text{CO}_3$ - extract + $\text{FeCl}_3$	Red colouration	$\text{CH}_3\text{COO}^-$ confirmed
3	Solid mixture + dil. $\text{H}_2\text{SO}_4$ $\xrightarrow{\text{Heat}}$	Vinegar like smell	$\text{CH}_3\text{COO}^-$ confirmed

Tests for  $\text{ClO}_3^-$ 

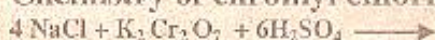
No	Experiments	Observations	Inferences
1	Acidified $\text{Na}_2\text{CO}_3$ - extract + KI sol. + Starch sol.	Blue colour	$\text{ClO}_3^-$ confirmed
2	Neutral $\text{Na}_2\text{CO}_3$ - extract + $\text{AgNO}_3$ sol. + few crystals of $\text{NaNO}_2$	White ppt. soluble in $\text{NH}_3$	$\text{ClO}_3^-$ confirmed
3	Acidified $\text{Na}_2\text{CO}_3$ - extract + Few drops of aniline sulphate + conc. $\text{H}_2\text{SO}_4$ along the walls of test tube	A deep blue colour or ring formed	$\text{ClO}_3^-$ confirmed

## Tests for similar radicals in presence of each other:

1.  $\text{Br}^-$  in presence of  $\text{I}^-$ :

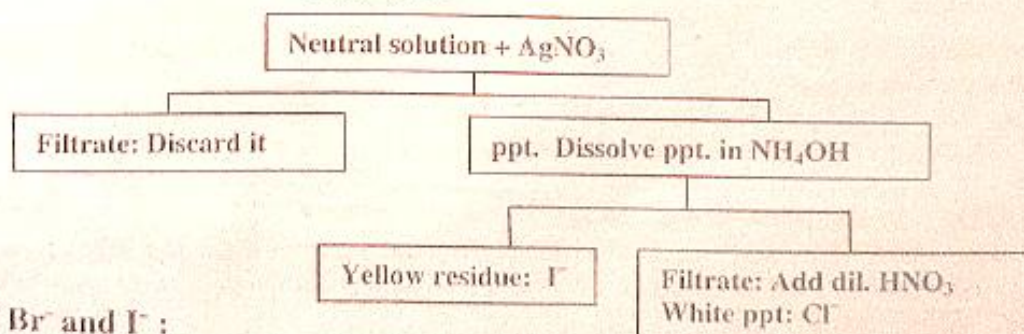
To the neutral  $\text{Na}_2\text{CO}_3$  - extract add  $\text{CS}_2$  and chlorine water dropwise and shake well. Violet colour imparted to  $\text{CS}_2$  layer indicates the presence of  $\text{I}^-$ . Add more chlorine water, if the violet colour changes to brown,  $\text{Br}^-$  is present. If violet colour becomes colourless,  $\text{Br}^-$  is absent. Chloride does not interfere if present.

## Chemistry of chromyl chloride test

2.  $\text{Cl}^-$  in the presence of  $\text{I}^-$ :

To 1-2 mL of neutral  $\text{Na}_2\text{CO}_3$  - extract add 1-2 mL of  $\text{AgNO}_3$  solution. Filter and reject the filtrate. Treat the ppt with  $\text{NH}_4\text{OH}$  and filter. A yellow residue indicates the presence of  $\text{I}^-$ . Add dil.  $\text{HNO}_3$  to the filtrate, a white ppt. shows the presence of presence of  $\text{Cl}^-$

## Flow sheet

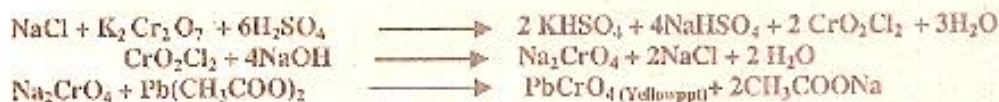
3.  $\text{Cl}^-$  in the presence of  $\text{Br}^-$  and  $\text{I}^-$ :

Chloride gives Chromyl chloride Test and bromide & iodide do not interfere if present.

Chromyl chloride test: Solid mixture + $\text{K}_2\text{Cr}_2\text{O}_7$ + Conc. $\text{H}_2\text{SO}_4$ $\xrightarrow{\text{Heat}}$ pass the vapours ( $\text{CrO}_2\text{Cl}_2$ ) in a test tube containing $\text{NaOH}$ solution; acidify with acetic acid + $\text{Pb}(\text{CH}_3\text{COO})_2$ solution dropwise	A thick yellow ppt. formed	$\text{Cl}^-$ confirmed
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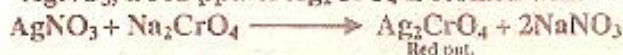
## Notes / Explanation:

4.  $\text{Cl}^-$  in the presence of  $\text{Br}^-$ 

Apply Chromyl chloride test to detect  $\text{Cl}^-$ . To  $\text{Na}_2\text{CO}_3$  - extract add  $\text{CS}_2$  and chlorine water with constant shaking. A brown colouration indicates presence of  $\text{Br}^-$ .

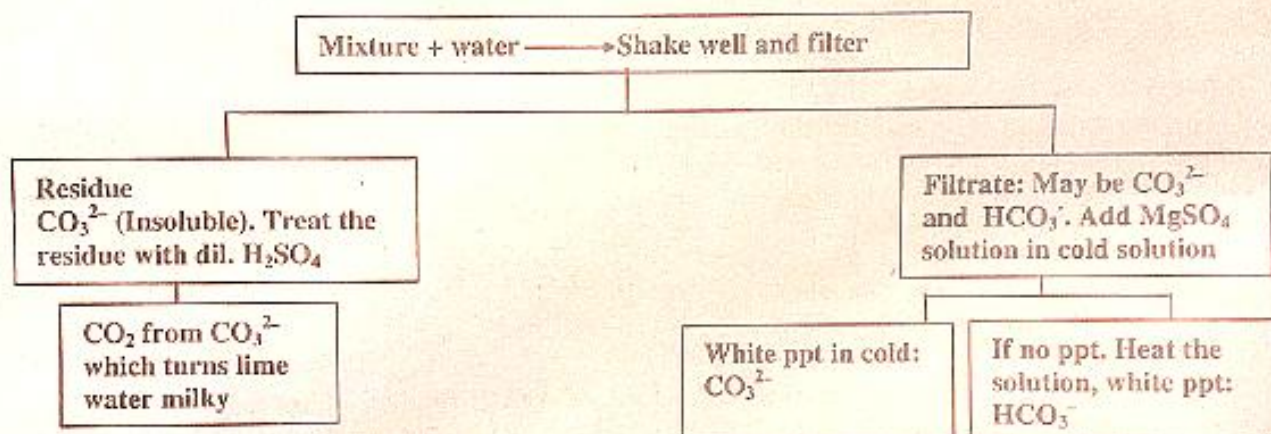
5.  $\text{Cl}^-$  in the presence of  $\text{CrO}_4^{2-}$ 

- Apply Apply Chromyl chloride test for chloride.
- Add  $\text{AgNO}_3$  to neutral  $\text{Na}_2\text{CO}_3$  - extract which give white ppt. due to chloride. Continue adding  $\text{AgNO}_3$ , a red ppt. of  $\text{Ag}_2\text{CrO}_4$  is formed which confirms  $\text{CrO}_4^{2-}$ .

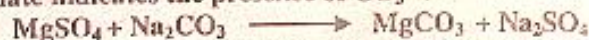
6.  $\text{CO}_3^{2-}$  in the presence of  $\text{HCO}_3^-$ :

Carbonates of alkali metals except Li are water soluble while carbonates of other, metals are insoluble. Bicarbonates of metals are soluble in water. If both  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  are present in the mixture, dissolve about 0.5 g of the mixture in water and filter. Treat both filtrate and residue as given in the following flow sheet.

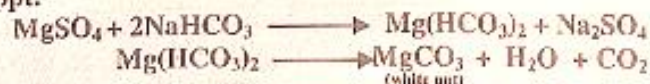
## Flow sheet



Notes / Explanations: Formation of white ppt. in cold on addition of  $\text{MgSO}_4$  to the solution containing carbonates and bicarbonate indicates the presence of  $\text{CO}_3^{2-}$ .

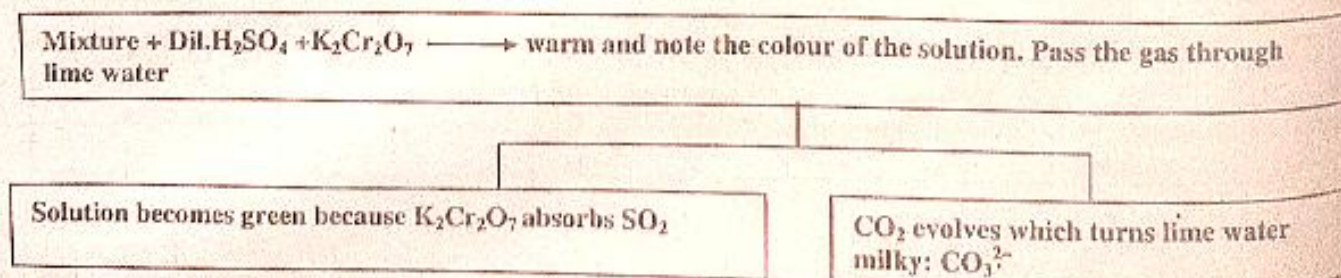


Bicarbonates are soluble and do not give ppt. On heating the solution, bicarbonates decompose to give carbonates which form ppt.

7.  $\text{CO}_3^{2-}$  in the presence of  $\text{SO}_3^{2-}$ 

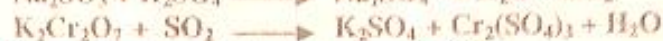
Both  $\text{CO}_3^{2-}$  and  $\text{SO}_3^{2-}$  react with dil.  $\text{H}_2\text{SO}_4$  and produce  $\text{CO}_2$  and  $\text{SO}_2$  which turns lime water milky. Therefore one must be eliminated to test the other. Follow the procedure given in the chart below.

## Flow sheet

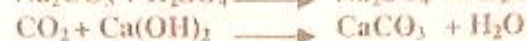
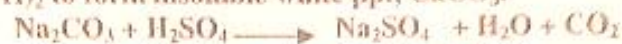




**NOTES/ EXPLANATIONS:** Sulphites reacts with dil.  $\text{H}_2\text{SO}_4$  to give  $\text{SO}_2$  which reacts with  $\text{K}_2\text{Cr}_2\text{O}_7$  and solution becomes green due to formation of  $\text{Cr}_2(\text{SO}_4)_3$ .



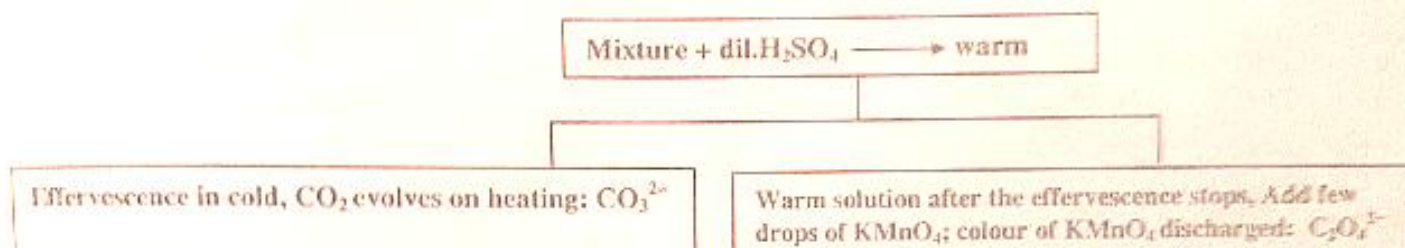
$\text{CO}_2$  react with lime water,  $\text{Ca}(\text{OH})_2$  to form insoluble white ppt,  $\text{CaCO}_3$ .



### 8. $\text{CO}_3^{2-}$ in the presence of $\text{C}_2\text{O}_4^{2-}$

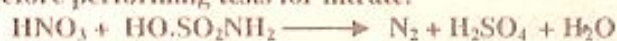
Carbonates react with dil.  $\text{H}_2\text{SO}_4$  to yield  $\text{CO}_2$  which turns lime water milky. Heat the solution to decompose the carbonate completely. Add few drops of  $\text{KMnO}_4$  to this warm solution. Decolourization of  $\text{KMnO}_4$  indicates the presence of oxalates.

#### Flow sheet



### 9. $\text{NO}_2^-$ in the presence of $\text{NO}_3^-$

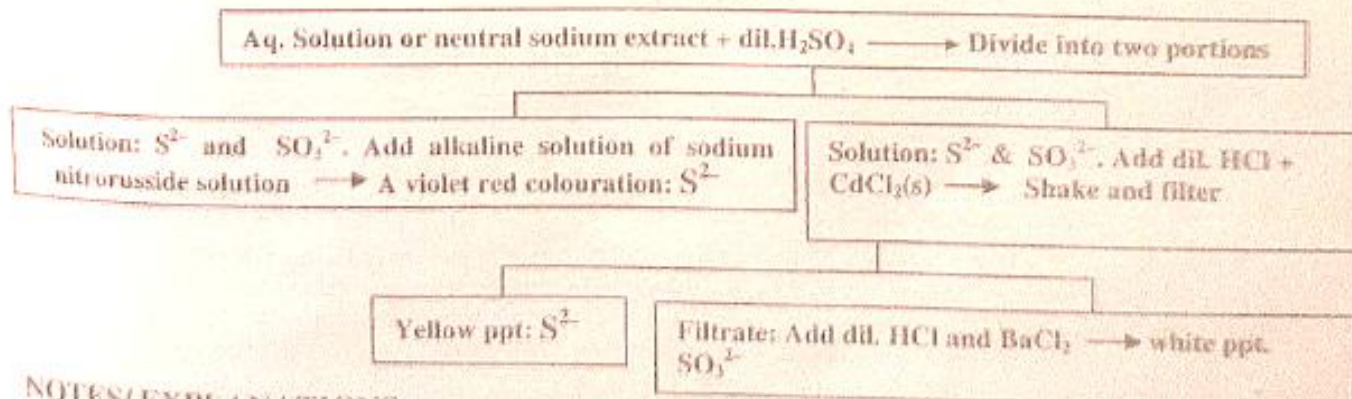
Nitrite can be detected in the presence of nitrate by usual tests like Ring test but nitrate cannot be detected in the presence of nitrite. Therefore nitrite is decomposed by adding sulphamic acid to the acidified solution of the mixture before performing tests for nitrate.



### 10. $\text{S}^{2-}$ in the presence of $\text{SO}_3^{2-}$

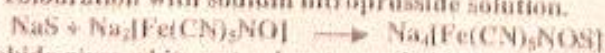
Dissolve the mixture in water or prepare  $\text{Na}_2\text{CO}_3$ -extract and neutralize it with dil.  $\text{H}_2\text{SO}_4$ . Divide this solution into two portions. To one portion add few drops of sodium nitroprusside solution. A violet red colouration indicates the presence of  $\text{S}^{2-}$ . To the second portion add dil.  $\text{HCl}$ , solid  $\text{CdCO}_3$ , shake vigorously and filter, yellow ppt. indicate  $\text{S}^{2-}$ . Acidify the filtrate with add dil.  $\text{HCl}$  and add  $\text{BaCl}_2$  and bromine water. A white ppt. shows the presence of  $\text{SO}_3^{2-}$ .

#### Flow sheet

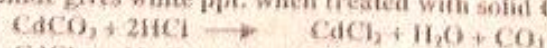


#### NOTES/ EXPLANATIONS

Sulphide gives violet red colouration with sodium nitroprusside solution.



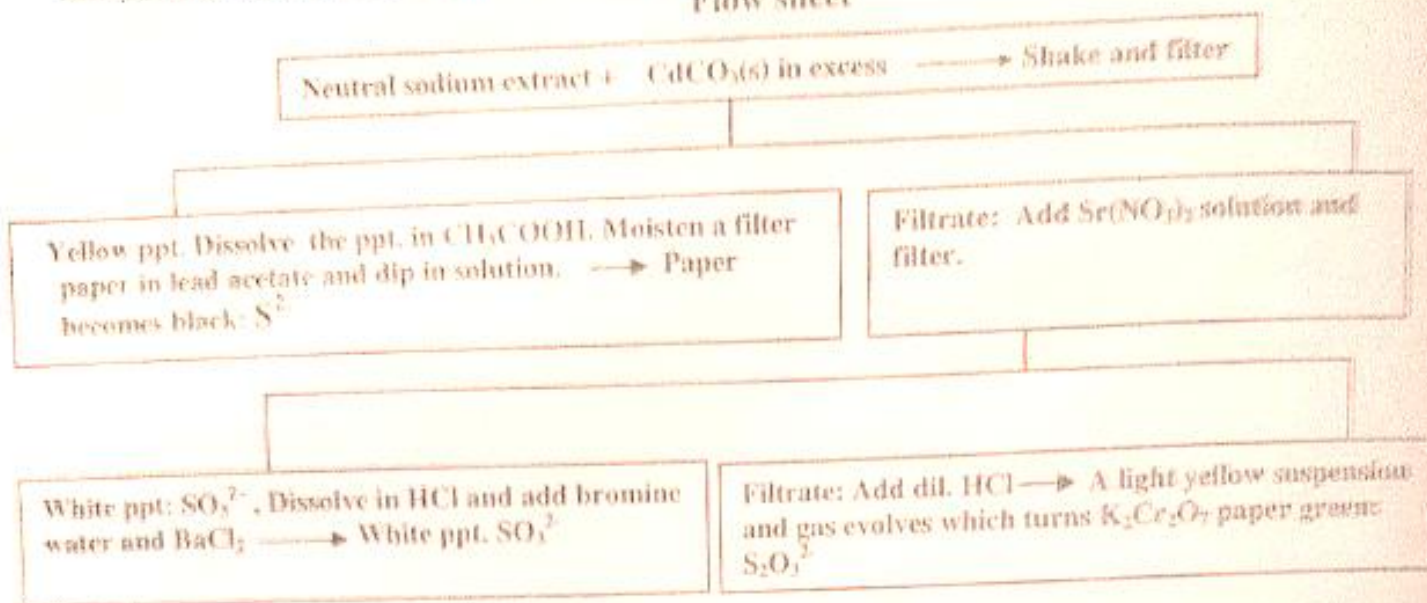
Acidified solution of sulphide gives white ppt. when treated with solid  $\text{CdCO}_3$ .





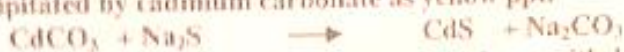
11.  $S^{2-}$ ,  $SO_3^{2-}$ ,  $S_2O_3^{2-}$ , in the presence of each other  
Analyze these cations according to the following scheme.

## Flow sheet



## NOTES/ EXPLANATIONS

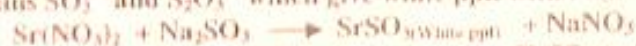
1. Sulphide is precipitated by cadmium carbonate as yellow ppt.



Ppt. is dissolved in dil. acetic acid. A piece of filter paper moisten with lead acetate solution is dipped in the solution. Filter paper becomes black



2. Filtrate may contain  $SO_3^{2-}$  and  $S_2O_3^{2-}$  which give white ppt. with  $Sr(NO_3)_2$  solution

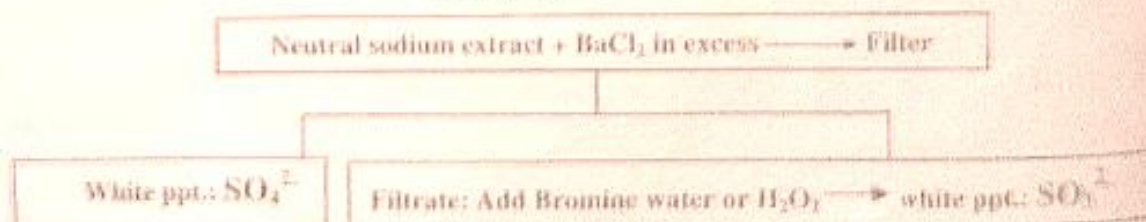


$SrSO_3$  is dissolved in dil. HCl and bromine water is added to oxidize  $H_2SO_3$  to  $H_2SO_4$  which reacts with  $BaCl_2$  to form white ppt.

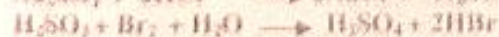
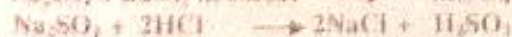


12.  $SO_3^{2-}$  in the presence of  $SO_4^{2-}$   
Analyze these cations according to the following scheme.

## Flow sheet



## NOTES/ EXPLANATIONS



13.  $SO_3^{2-}$  in the presence of  $S_2O_3^{2-}$

Add dil HCl to the aq. solution of the mixture. A light yellow suspension shows the presence of sulphur. Filter and add bromine water and  $BaCl_2$  to filtrate. A white ppt. confirms thiosulphate.

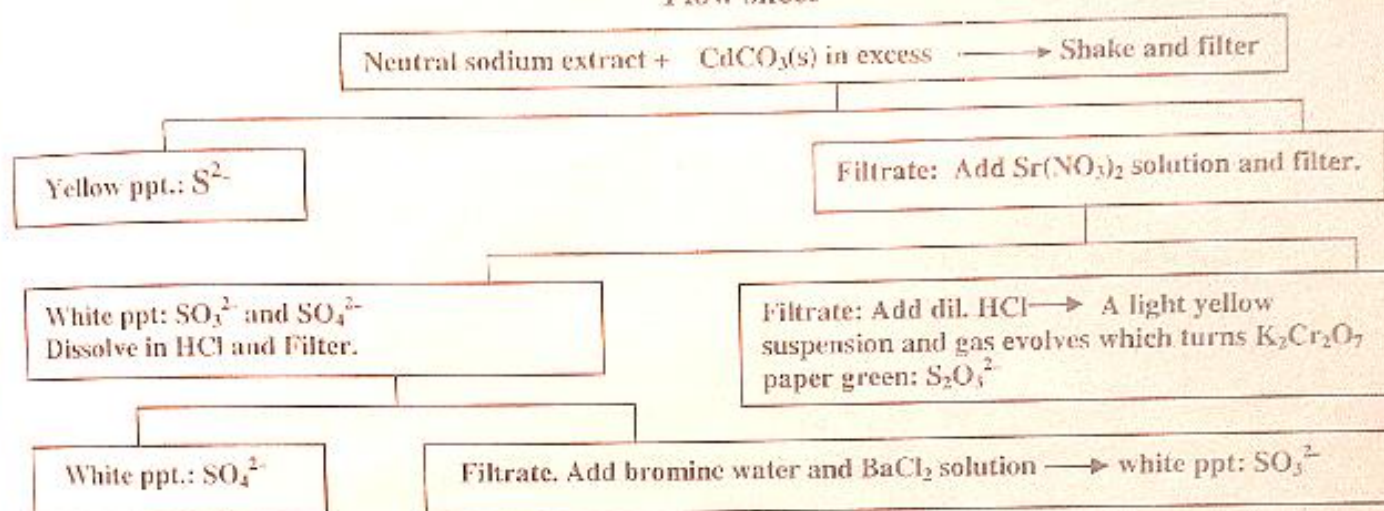


## NOTES/ EXPLANATION

14.  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{S}^{2-}$  in the presence of each other

Analyze these anions according to the following chart.

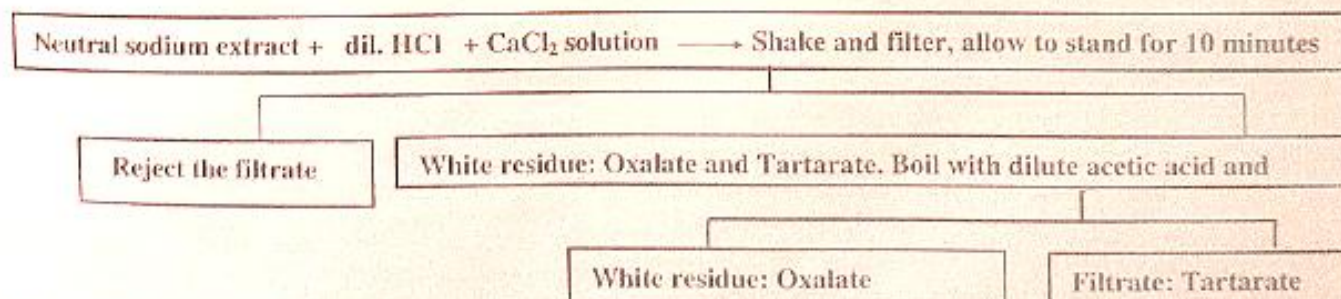
## Flow sheet

15.  $\text{CO}_3^{2-}$ ,  $\text{C}_2\text{O}_4^{2-}$  and tartarate in the presence of each other

Analyze these anions as follows:

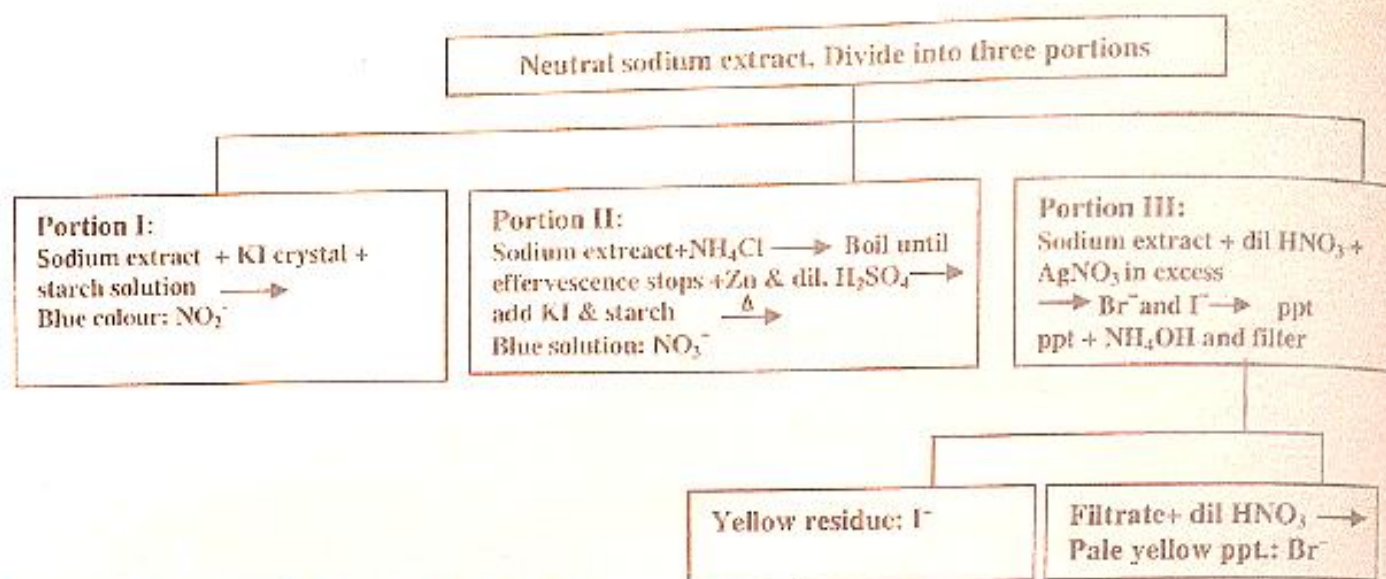
- Add dil.  $\text{H}_2\text{SO}_4$  to solid mixture in a test tube. Evolution of  $\text{CO}_2$  with effervescence, which turns lime water milky, indicates the presence of  $\text{CO}_3^{2-}$ .
- Add conc.  $\text{H}_2\text{SO}_4$  to solid mixture in a test tube. Blackening of the contents indicates the presence of tartarate.
- Acidify the neutral  $\text{Na}_2\text{CO}_3$  - extract with dil HCl and boil the solution to remove the  $\text{CO}_2$ . Add  $\text{CaCl}_2$  solution and allow to stand for 10 minutes and filter. Reject the filtrate and analyze as follows.

## Flow sheet

16.  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  in the presence of each other

Nitrite produces blue colour with KI and starch. Nitrate can be reduced to nitrite by treatment with Zn and dilute  $\text{H}_2\text{SO}_4$  and subsequently tested with KI and starch. Bromide and iodide give ppt. with  $\text{AgNO}_3$  which can be separated due to solubility of  $\text{AgBr}$  in  $\text{NH}_4\text{OH}$ . The scheme of analysis is shown in the chart.





### 17. $\text{NO}_3^-$ and $\text{NO}_2^-$ present together:

Nitrite is first removed by heating the  $\text{Na}_2\text{CO}_3$  -extract with  $\text{NH}_4\text{Cl}$  and nitrate is detected with usual ring test or KI and starch solution.

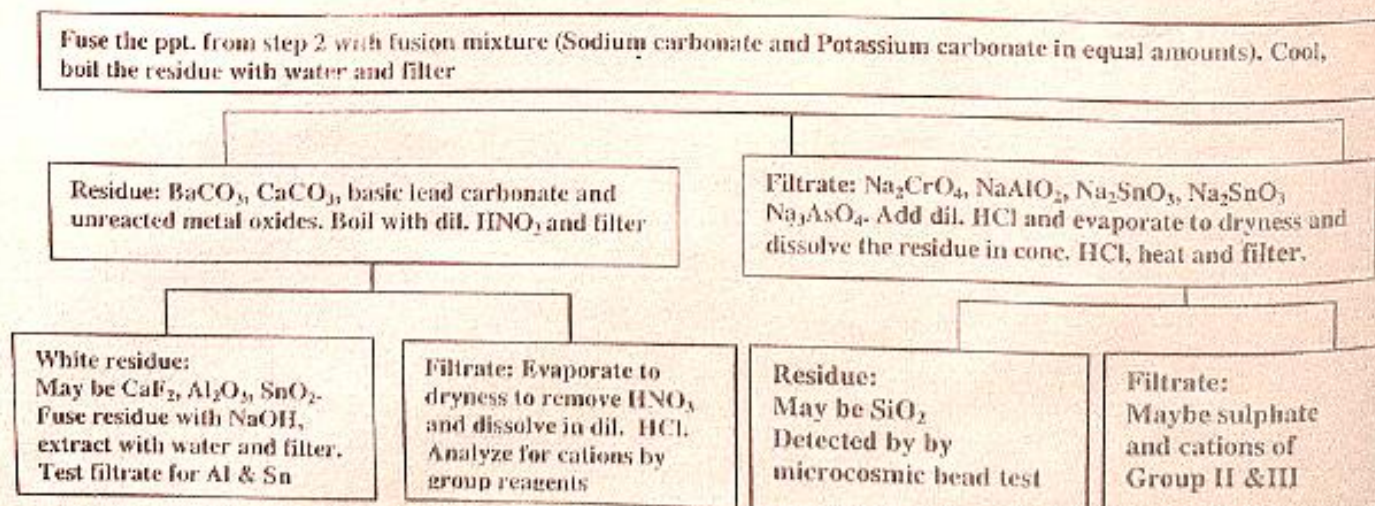
Sodium extract +  $\text{NH}_4\text{Cl}$  → Boil until effervescence stops + Zn & dil.  $\text{H}_2\text{SO}_4$  → add KI & starch  
→ Blue solution:  $\text{NO}_3^-$

## Scheme of Analysis for Insoluble substances

Substance which are insoluble even in aqua regia are treated as *insoluble* substances; these include  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{AgCN}$ , oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{SnO}_2$ ,  $\text{Sb}_2\text{O}_3$ , ferro and ferricyanides of Fe, Ni, Cu,  $\text{CaF}_2$ , silicates etc. Following scheme of analysis would be helpful for the students.

1. Stir up the mixture with ammonium acetate solution and filter. Sulphates of Pb, Ba and Sr will go into solution which can be tested with usual testes.
2. Heat the residue with Zn and dil.  $\text{H}_2\text{SO}_4$ . Silver salts are reduced to silver and soluble Zn salts are formed. Filter and test the filtrate for halogen and cyanides. Dissolve the ppt. in  $\text{HNO}_3$  and filter. Filtrate may contain  $\text{AgNO}_3$  which can be tested with dil. HCl. Analyze the residue according to the flow sheet.

### Flow sheet





## Scheme of Analysis of Basic Radicals:

Inorganic substances are analyzed qualitatively through dry and wet tests. Systematic qualitative analysis of basic radicals may comprise of the following steps.

a. Preliminary Examination of the mixture.

b. Identification of basic radicals through dry and wet tests:

Dry tests are performed on solid substances. If solid salt is not provided, evaporate the solution to get the solid salt. Dry tests may be performed for acid and basic radicals. Chemical tests or wet tests are performed on solution of the substance.

### Preliminary examination of salt

Preliminary examination of the salt consists of the following steps.

i. Examining the colour of salt.

ii. Examining the appearance of the salt.

Table 2.1: Colours of salts

iii. Smelling the odour.

i. Heating the dry salt.

ii. Dry tests

i. Colours of salts

Observe the colours of the mixture.

Colour of the salt gives important information about the cation (basic radical) of the mixture. Identify the cations from the colour of the salt as given in the table. Colours of the salt solutions are given in the figure.

ii. Appearance of salt

Note the physical state of the salt and get preliminary information about the cations.

Observations	Inferences
Blue or Bluish green; if green turns blue on dilution	$\text{Cu}^{2+}$
Light pink	$\text{Mn}^{2+}$
Dark pink	$\text{Co}^{2+}$
Light green or colourless on dilution	$\text{Fe}^{2+}$
Bright green	$\text{Ni}^{2+}$
Yellow or brown	$\text{Fe}^{3+}$
Dark green or purple	$\text{Cr}^{3+}$
Yellow; turns orange on addition of an acid	$\text{Cr}_2\text{O}_7^{2-}$
Orange; turns yellow on addition of an alkali	$\text{Cr}_2\text{O}_7^{2-}$
Dark violet or blue with metallic luster	$\text{MnO}_4^{2-}$
Pale yellow, solution colourless	$[\text{Fe}(\text{CN})_6]^{4-}$
Ruby red	$[\text{Fe}(\text{CN})_6]^{3-}$
White or colourless	Above radicals absent

Table 2.2: Physical states of some common compounds

Observations	Inferences
1. Amorphous	2nd and 3 <sup>rd</sup> group metal oxalates, phosphates & carbonates present.
2. Crystalline	May be $\text{Pb}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Ba}^{2+}$
3. Light powder	May be carbonates or phosphates of $\text{Mg}^{2+}$ , $\text{Zn}^{2+}$ or $\text{Bi}^{3+}$
4. Salt is deliquescent	May be Halides of $\text{Zn}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Sb}^{3+}$ , $\text{Al}^{3+}$ and $\text{Fe}^{3+}$

iii. Odour (smell):

Smell the salt carefully and record information.

iv. Dry Heating

Heat a small quantity of the given salt in a dry and clean test tube first gently and then strongly and observe the following carefully.

1. Change in the state of the salt.

2. A sublimate is formed.

3. Evolution of any gas.

4. Change in colour of the residue.

1. Change in state

Table 2.3: Odour of some common salts

No	Observations	Inferences
1.	Smell of ammonia	$\text{NH}_4^+$ indicated
2.	Rotten egg smell	$\text{S}^{2-}$ indicated
3.	Vinegar like smell	$\text{CH}_3\text{COO}^-$ indicated
4.	Bitter almond	$\text{CN}^-$ indicated
5.	Chlorine like	hypochlorite indicated



Table 2.4: Change in states of solid salts on heating.

No	Observations	Inferences
(i)	Salt swells up.	$\text{PO}_4^{3-}$ or alums or borates indicated
(ii)	The substance decrepitates and gives crackling sound.	$\text{NaCl}$ , $\text{KCl}$ , $\text{KBr}$ , $\text{Pb}(\text{NO}_3)_2$ or $\text{KI}$ .
(iii)	Water condensation occurs.	Hydrated salts indicated
(iv)	Violet vapours evolve.	$\text{I}^-$ indicated
(v)	The substance fuses.	Salts of alkali metals and hydrated salts.

### Explanations/ Notes

Salts containing water of crystallization swells up on heating due to evolution of water, e.g.,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  and  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$

Some substances like  $\text{NaCl}$  and  $\text{Pb}(\text{NO}_3)_2$  contain small quantities of mother liquor in their crystals. These substances fly to pieces with crackling sound due to evolution of entrapped moisture.

Hydrated salts like halides (of Fe, Co, Ni, and Ca), sulphates (of Na, Mg, Zn) and nitrates (of Fe, Co, Zn, Ni, Cu) lose water of crystallization on heating.

Iodides in presence of oxygen liberate iodine vapours which condense on the cooler parts of the test tubes as  $\text{I}_2$  crystals.



Halides of Na, K, Sn, Pb, Sb, Bi, nitrates of alkali and alkaline earth metals, chromates, acetates, and alkali hydrogen sulphate fuse to form solid residue.

Table 2.5: Colours of sublimate

Colour of sublimate	Inference
(i) White sublimate with smell of ammonia.	$\text{NH}_4^+$
(ii) White sublimate with no smell.	$\text{HgCl}_2$
(iii) Yellow sublimate.	$\text{Hg}_2\text{Cl}_2$ $\text{HgI}_2$ , $\text{As}_2\text{O}_3$ $\text{As}^{3+}$
(iv) White sublimate with garlic like smell.	$\text{Hg}^{2+}$
(v) Grey sublimate.	$\text{Br}^-$
(vi) Brown oily drops with suffocating smell.	
(vii) Black sublimate, violet vapours.	$\text{I}^-$

1. A sublimate is formed: Some salts directly changes into vapours on heating and these vapours condense
2. on cooler part of the tube; the process is called sublimation and substance condensed is called sublimate. Table 2.5 shows the information obtained from this treatment.

#### Evolution of any gas?

Some compounds decompose on heating and give off characteristic gases. The gases may be:

- a. Colourless and odourless
- b. Colourless with odour
- c. Coloured gases with characteristic odour
- d. Mixture of gases or vapours

#### a. Colourless and odourless gases

Table 2.6: Information obtained from evolution of Colourless and odourless gases evolved on heating.

Observations	Inference
Oxygen evolved (rekindles glowing splinter or burning match stick)	$\text{NO}_3^-$ , oxides, chlorates, bromates, permanganates and iodates.
$\text{CO}_2$ gas comes out with effervescence turns lime water milky, extinguishes burning match stick.	$\text{CO}_3^{2-}$ or $\text{HCO}_3^-$ , $\text{C}_2\text{O}_4^{2-}$ and hydroxy acids.
A gas burns with blue flame( $\text{CO}$ gas)	Carbonates, Formates and oxalates
Colourless gas does not turn lime water milky( $\text{N}_2$ gas)	$\text{NH}_4\text{NO}_3$ , $(\text{NH}_4)_2\text{CrO}_4$ , $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
Acetone vapours, inflammable.	Condensable acetates

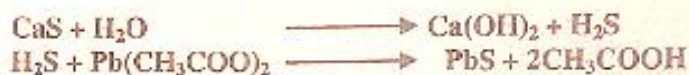


## b. Colourless gases with odour

Observations	Inference
Rotten egg smell, turns lead acetate paper black ( $\text{H}_2\text{S}$ )	$\text{S}^{2-}$ and $\text{S}_2\text{O}_3^{2-}$ indicated
Pungent and irritating smell, turns blue litmus red and gives dense white fumes with $\text{NH}_4\text{OH}$ ( $\text{HCl}$ gas)	$\text{Cl}^-$ (Hydrated chlorides) indicated
Ammonia like smell, gives white fumes with $\text{HCl}$ , turns turmeric paper brown ( $\text{NH}_3$ gas)	$\text{NH}_4^+$ indicated
Smell like burning sulphur, turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper green ( $\text{SO}_2$ ) (Colour of the contents remained unchanged)	$\text{SO}_3^{2-}$ indicated
Smell of burning sulphur, turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper green and colour of the contents turned yellow. ( $\text{SO}_2$ gas)	$\text{S}_2\text{O}_3^{2-}$ indicated
Vinegar like smell turns blue litmus paper red (vapours of $\text{CH}_3\text{COOH}$ )	$\text{CH}_3\text{COO}^-$ indicated
White pungent fumes turns blue litmus paper red ( $\text{SO}_3$ gas)	Sulphates indicated

## Explanations/ Notes

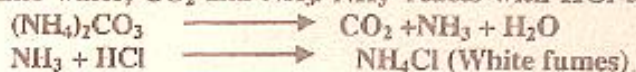
Sulphides and thiosulphates decompose to give  $\text{H}_2\text{S}$  on heating.  $\text{H}_2\text{S}$  reacts with lead acetate to form  $\text{PbS}$  (Black colour).



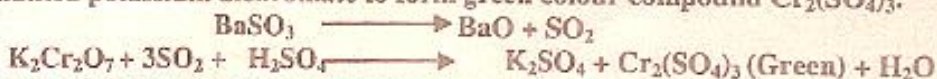
Hydrated chlorides on heating give a colourless gas with pungent smell. It is  $\text{HCl}$  gas which produces dense white fumes with  $\text{NH}_4\text{OH}$ .



For example ammonium carbonate decomposes into water,  $\text{CO}_2$  and  $\text{NH}_3$ .  $\text{NH}_3$  reacts with  $\text{HCl}$  to give white dense fumes.

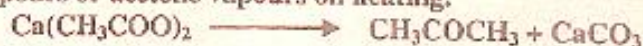


Sulphites, thiosulphates and some sulphates undergo decomposition on heating and evolve  $\text{SO}_2$  with strong pungent smell.  $\text{SO}_2$  reacts with acidified potassium dichromate to form green colour compound  $\text{Cr}_2(\text{SO}_4)_3$ .



Thiosulphates decompose to give free sulphur which turns the contents yellow.

Acetates decompose to give acetic acid vapours or acetone vapours on heating.



Some sulphates decompose on heating and release  $\text{SO}_3$



## c. Coloured gases with characteristic odour

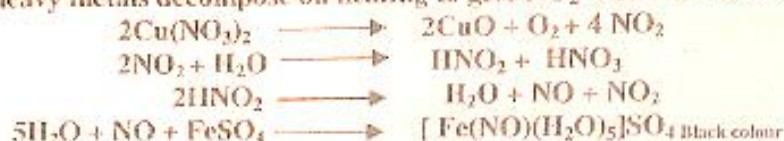
Colour of the gases, odour of the gases and corresponding radicals are given in the table.

Observations	Inference
Reddish brown gas, gives orange red solution when passed into water, has irritating smell; bleaches the litmus paper ( $\text{Br}_2$ gas)	$\text{Br}^-$ indicated
Reddish brown gas, turns $\text{FeSO}_4$ paper black (evolves briskly when a paper pellet is put into test tube); $\text{NO}_2$ gas.	$\text{NO}_2^-$ or $\text{NO}_3^-$ indicated
Greenish yellow gas, with pungent smell, bleaches litmus paper and turns KI-starch paper blue. ( $\text{Cl}_2$ )	$\text{Cl}^-$ indicated
Violet gas, turns starch paper blue. ( $\text{I}_2$ vapours)	$\text{I}^-$ indicated



## Explanations/ Notes

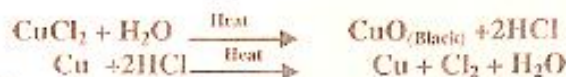
Nitrites and nitrates of heavy metals decompose on heating to give  $\text{NO}_2$  which turns  $\text{FeSO}_4$  solution black.



Bromides give bromine gas on heating which have choking smell and bleaches the litmus paper. It dissolves in water forming orange red solution.



Chlorides of some metals which form oxidizing oxides release greenish yellow  $\text{Cl}_2$  gas. This gas bleaches moist litmus paper.



Iodides liberates when heated in the presence of oxidizing agents.

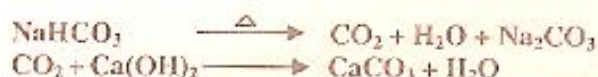


## c. Mixture of gases or vapours

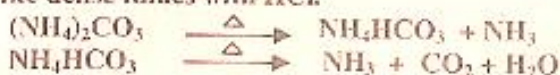
Observations	Inferences
i. Carbon dioxide and water vapours	Alkali metal bicarbonates or hydroxy carbonates.
ii. Carbon dioxide and ammonia vapours	Ammonium carbonates or bicarbonates.
iii. Iodine or bromine or chlorine and oxygen gas.	Heavy metal iodates, bromates or chlorates

## Explanations/ Notes

Alkali metal bicarbonates or hydroxy carbonates decompose on heating and produce  $\text{H}_2\text{O}$  and  $\text{CO}_2$  which turns lime water milky



Ammonium carbonates or bicarbonates decompose to give carbon dioxide and ammonia vapours which turns lime water milky and produce white dense fumes with  $\text{HCl}$ .



Heavy metal iodates, bromates or chlorates decompose thermally to give iodine or bromine or chlorine and oxygen gas.



## Change in the colour of residue

Change in the colour of residue	Inferences
i. Residue is black with charring, salt is colourless.	$\text{C}_2\text{O}_4^{2-}$ , $\text{CH}_3\text{COO}^-$
ii. Residue white, salt is blue.	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
iii. Yellow on heating, dirty white in cold.	$\text{Sn}^{2+}$
iv. Yellow on heating, white in cold.	$\text{Zn}^{2+}$
v. Brown when hot, yellow when cold.	$\text{Pb}^{2+}$ , $\text{Bi}^{3+}$
vi. Black on heating, red in cold.	$\text{Hg}^{2+}$ , $\text{Fe}^{3+}$

## 2.4.2 Dry Tests

Chemical tests performed with the solid salts are called dry tests. These include charcoal cavity test, flame test, borax bead test and filter ash test.



# Colour Scheme for Salt Analysis

## 1. Colours of Salts



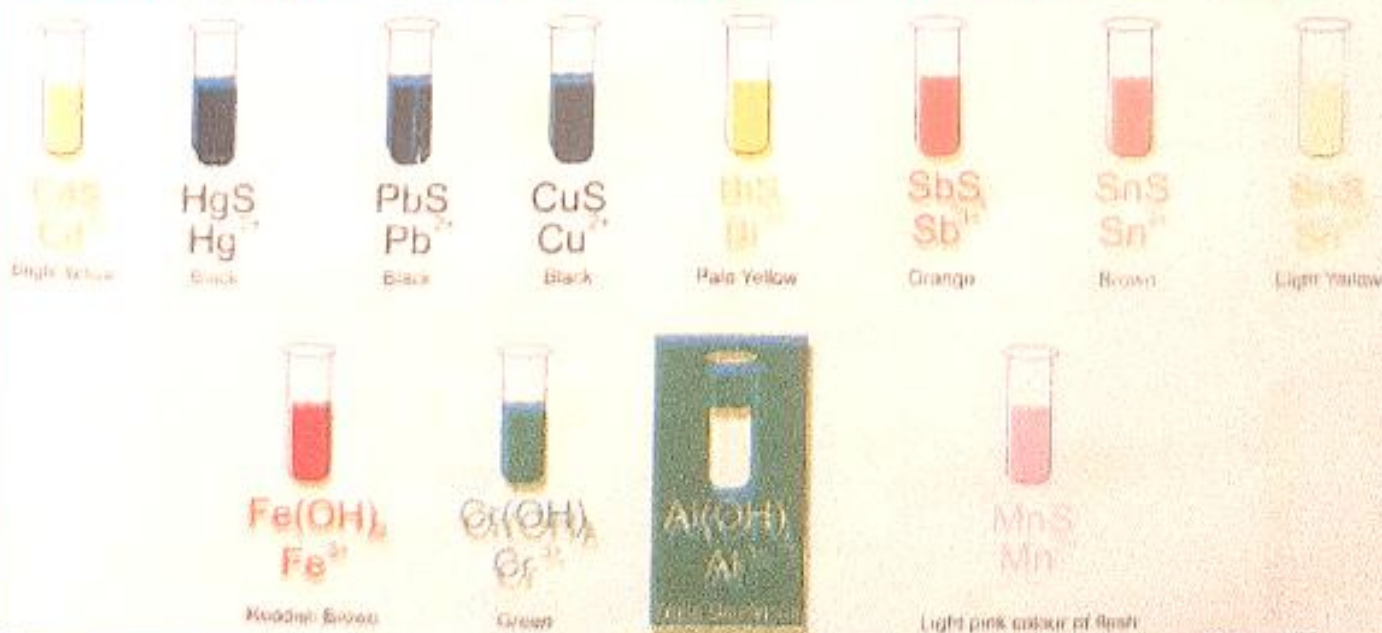
## 2. Colours of flames when salts, with conc. HCl are heated in outer side of flame of Bunsen burner



## 3. Colours of ashes of Filter Ash Test





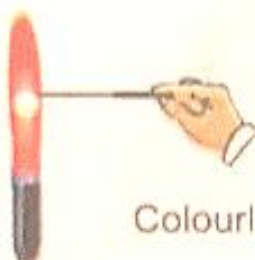

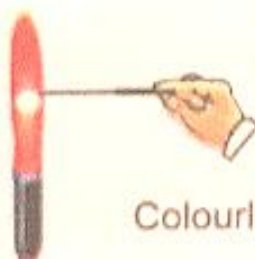







## 4. Colours of ppt. of basic radicals formed with Group Reagents.





## Colours of Beads of Borax Bead Test.

Colours of the hot Beads in the Inner Reducing Flame	Colours of the hot Beads in the Outer Oxidizing Flame	Indicated Radicals
 <p>Grey/ Black</p>	 <p>Reddish Brown</p>	$\text{Ni}^{2+}$
 <p>Colourless</p>	 <p>Violet</p>	$\text{Mn}^{2+}$
 <p>Colourless</p>	 <p>Green</p>	$\text{Cu}^{2+}$
 <p>Colourless</p>	 <p>Blue</p>	$\text{Co}^{2+}$
 <p>Green</p>	 <p>Yellow</p>	$\text{Fe}^{3+}$
 <p>Deep Green</p>	 <p>Deep Green</p>	$\text{Cr}^{3+}$



### a. Charcoal Cavity Test

**Procedure:** Mix 1 g of the given salt, 1 g  $\text{Na}_2\text{CO}_3$  and 2 g  $\text{K}_2\text{CO}_3$  and fill the cavity of charcoal block with this mixture. Put a drop of water on the mixture to make it compact.

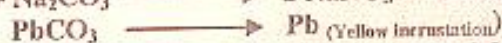
(2) Take a burner with air hole closed and place a blow pipe in the centre of the flame and hold the charcoal block in slanting position. Blow gently and note the bead scale or incrustation formed as given below:

Table 2.6: Observations and inferences of charcoal cavity test

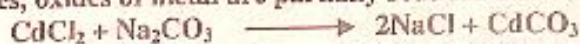
Observations		Inferences
a.	White bead which marks the paper and yellow incrustation.	$\text{Pb}^{2+}$
b.	White malleable bead does not mark the paper.	$\text{Ag}^+$
c.	Dark brown incrustation and no bead.	$\text{Cd}^{2+}$
d.	Red scale but no bead or incrustation.	$\text{Cu}^{2+}$
e.	Yellow incrustation when hot and white when cold, no bead.	$\text{Zn}^{2+}$
f.	Orange yellow incrustation.	$\text{Bi}^{3+}$
g.	White brittle bead which gives fumes when heated. White incrustation on the boundary of the flame.	$\text{Sb}^{3+}$
h.	White malleable bead, yellow when hot, white when cold	$\text{Sn}^{2+}$
i.	Dark residue.	$\text{Fe}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Mn}^{2+}$

### Explanations/ Notes

When base holes of the burner are closed, it produces yellow coloured reducing flame which has un-burnt carbon particles due to incomplete combustion of gas. Moreover, charcoal cavity also provides carbon particles. The salts react with mixture ( $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in 1:2 ratios) and carbonates of the metals are formed. Carbonates of the metals decompose to form metal oxides. The metal oxides are reduced in certain cases by carbon particles of the flame or charcoal. The metal is given up either as beads, or in the form of scales or incrustation. A bead means spherical particle of the metal. Metal having low melting point form bead like lead. An incrustation is a layer of oxides formed at the brim of the cavity. Metal having high melting points are given out as scale as in case of copper. For example the salt is  $\text{Pb}(\text{NO}_3)_2$ , so,



In certain cases, oxides of metal are partially reduced and we get incrustations only e.g.



$\text{Na}_2\text{CO}_3$  acts as flux and protects the bead formed.

### b. Filter Ash Test

#### Procedure

Prepare the solution of the given salt, dip a filter paper in this solution and dry it over the burner. Dip this filter paper in the solution of  $\text{Co}(\text{NO}_3)_2$  and ignite (burn) the paper. Note the colour of the ash and identify the radicals as given in table.

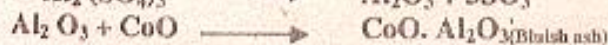
Colours of ash	Inference
Green	$\text{Zn}^{2+}$
Blue	$\text{Al}^{3+}$
Pink	$\text{Mg}^{2+}$
Bluish green	$\text{Sn}^{2+}$

### Explanations/ Notes

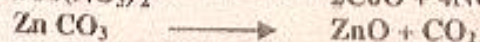
Salts of  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sn}^{2+}$  and  $\text{Mg}^{2+}$  when heated, decompose into their oxides. These oxides react with  $\text{CoO}$  formed by decomposition of  $\text{Co}(\text{NO}_3)_2$  and form the product (ash) of characteristic colour.

For example,

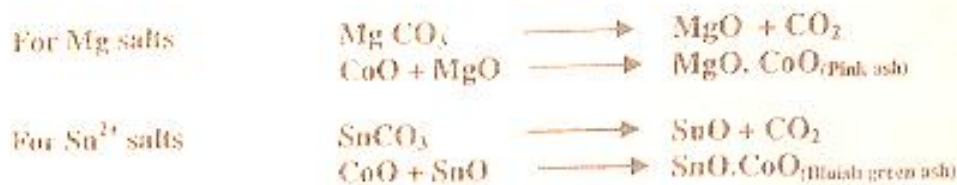
For  $\text{Al}^{3+}$  salts



For  $\text{Zn}^{2+}$  salts







### b. Borax Bead Test

#### What is borax bead test?

The bead test, sometimes called the borax bead or blister test, is an analytical method used to detect the presence of certain metals. The principle of the test is that oxides of these metals produce characteristic colours when exposed to a flame. The test is sometimes used to identify the metals in minerals. In this case, a mineral-coated bead is heated in a flame and cooled to observe its characteristic colour. This test is applicable to coloured salts only.

#### Procedure

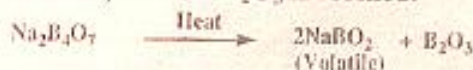
1. Take a clean platinum wire having a loop at its end. Dip the loop in conc. HCl and heat it in the flame repeatedly until it imparts no colour to the flame. Heat the loop in the flame and place it in powdered borax quickly.
2. Heat the loop carrying borax particles in the oxidizing flame until borax swells up, fuses and forms a colourless transparent glassy bead. If the bead is not colourless, reject it and try again.
3. Now, put the heated bead into the given powdered salt so that a few grains of the salt stick to the bead and again heat the bead, carrying salt particles, into reducing and oxidizing flames.
4. Use the table below as an identification guide. Notice that the colour of the head depends on the type of flame used, the temperature of the bead when examined, and the concentration of the solution (if a solution of salt is used instead of the solid salt).

Table 3.6: Colours of borax beads in borax bead test

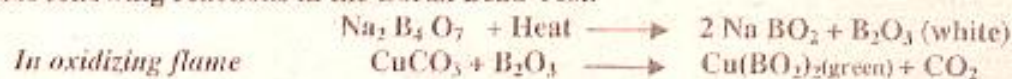
Colour of bead in oxidizing flame		Colour of bead in reducing flame		Inference
Colour of hot bead	Colour of cold bead	Colour of hot bead	Colour of cold bead	
(i) Reddish brown	Reddish brown	Grey / black	Grey / black	$\text{Ni}^{2+}$
(ii) Violet	Violet	Colourless	Colourless	$\text{Mn}^{2+}$
(iii) Green	Blue	Colourless	Opaque red	$\text{Cu}^{2+}$
(iv) Blue	Blue	Colourless	Colourless	$\text{Co}^{2+}$
(v) Yellow	Yellow	Green	Green	$\text{Fe}^{2+}$
(vi) Emerald green (deep green)	Emerald green (deep green)	Emerald green (deep green)	Emerald green (deep green)	$\text{Cr}^{3+}$

### Explanations / Notes

When platinum loop carrying borax is heated, bead of  $\text{B}_2\text{O}_3$  is formed.



$\text{B}_2\text{O}_3$  is non volatile and displaces more volatile acidic oxides from oxy-salts forming the metal borates. These are fusible and form coloured transparent beads. For example,  $\text{CuCO}_3$  undergoes following reactions in the Borax Bead Test.



### c. Flame Test

The flame test is used to visually determine the identity of an unknown metal of an ionic salt based on the characteristic colour the salt imparts to the flame of a Bunsen burner.



## Procedure

- (1) Make a paste of the given salt with conc. HCl. Take this paste onto a loop of the clean platinum wire and heat it in the oxidizing flame. Observe the colour imparted to flame with naked eye and through a blue glass.
- (2) For cleaning the platinum wire, dip it in conc. HCl and heat in the flame repeatedly until it imparts no colour to the flame.

N.B: If platinum wire is not available, nickel / chrome wire can be used.

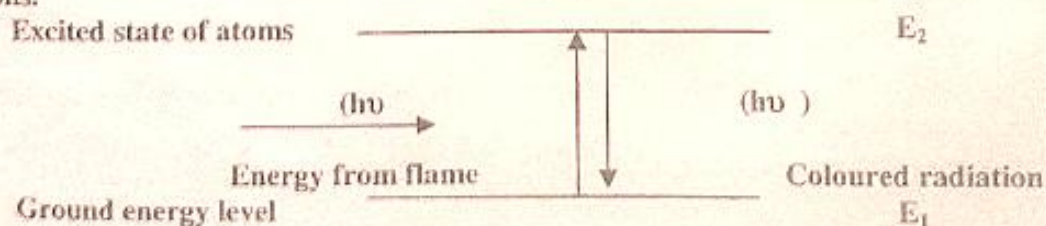
Table 3.7: Colours of flames in flame tests

Observations		Inferences
Colour of flame with naked eye	Colour of flame through blue glass.	
(i) Pale green	Green	$Ba^{2+}$ $Cu^{2+}$ $Na^+$ $Sr^{2+}$ $K^+$ $Ca^{2+}$
(ii) Greenish blue	-	
(iii) Golden yellow	Invisible	
(iv) Crimson (bright red)	Crimson (Bright red)	
(v) Violet	Crimson	
(vi) Orange red ((brick red)	Colourless	

## Explanations / Notes

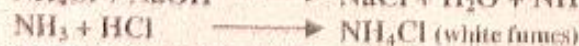
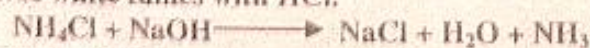
Salt is treated with conc. HCl to convert it into the chlorides because chlorides are the most volatile (and form vapours at lower temperature). The characteristic colour of the flame is due to metal ion and is not affected by acid radical. The metal atoms absorb radiant energy and their valence electrons go to higher energy levels i.e. atoms are excited. Excited atoms are unstable and electrons come to their ground level by emitting radiations which fall in visible region of spectrum and flame becomes coloured due to emitted radiations.

**IMPORTANT!** Check that your flame test wire is clean. Do this by holding the metal loop in the hottest part of the Bunsen burner flame. If it is clean, there should be no change in the colour of the flame when the metal loop is put in the flame. If the metal loop is not clean, clean it by dipping it into the concentrated hydrochloric acid provided, then holding the loop in the Bunsen burner flame. Repeat this cleaning until there is no more change in the colour of the flame.



### d. Test for Ammonium ( $NH_4^+$ )

**Procedure:** Heat 1g salt with NaOH solution. Smell of ammonia gas indicates the presence of  $NH_4^+$ . Ammonia gas gives white fumes with HCl.



$NH_4^+$  is confirmed by passing  $NH_3$  gas through Nessler's reagent which produces brown ppt.

e. **Reaction of sodium hydroxide with the salt/mixture:** Suspend about 30-50 mg of the mixture in a small quantity of water in a test tube and add to it NaOH solution dropwise in excess and boil it strongly. Note the evolution of ammonia; if ammonia gas is identified, mixture may contain ammonium salt ( $NH_4^+$ ). Boil the content till the evolution of ammonia gas stops. Now add a small piece of Devarda's alloy and heat the content again. Note the changes as given in the table.



Observations	Inference
Mixture is soluble in water and no ppt. with NaOH	Cations of the group I-V and $Mg^{2+}$ are absent.
Yellow ppt.	Chromium as chromate ( $CrO_4^{2-}$ )
Yellow solution	$[Fe(CN)_6]^{4-}$
Ammonium gas is evolved which produces white fumes with HCl	Ammonium salt $(NH_4)^+$ indicated
Ammonium gas is evolved with addition of Devarda's alloy	$NO_2$ and $NO$ indicated
$H_2$ gas is evolved	$Al^{3+}$ and $Zn^{2+}$ indicated

## Systematic Analysis of basic radicals by Wet tests

Chemical tests performed with the solutions of the salts are called wet tests. Solid salt is dissolved in suitable solvent and solution of salt is made to perform the wet tests. Solutions of salts for detection of acid and basic radicals are made by different methods.

Wet tests are performed with solution of the mixture and insoluble substances are treated separately.

### Preparation of original solution for basic radicals (o.s.)

Try to dissolve a little quantity of the mixture in solvent in the following order.

1. Water
2. Dil. HCl
3. Conc. HCl
4. Dil.  $HNO_3$
5. Conc.  $HNO_3$
6. Aqua regia (a mixture of one part conc.  $HNO_3$  and three parts conc. HCl.)

#### Procedure:

1. Take about 1.0 g of finely divided mixture in a 20 mL test tube and add 10 mL water. Boil it for 5 minutes. If the mixture gets dissolved, try to prepare more concentrated solution. If some residue is left behind, then filter and check the presence of solute in filtrate by evaporation. Use the aqueous solution for further analysis.
2. If the mixture is completely insoluble or partially soluble, take the mixture or the residue from 1 in another test tube, add dil. HCl and boil. If the mixture is completely soluble in dil. HCl, the radicals of Group I are absent and proceed for the next group.
3. If the mixture is partly soluble or insoluble, try to dissolve in conc. HCl. If the substance is soluble in conc. HCl, dilute with distilled water and proceed further. *If the solution is prepared in conc. HCl, most of the acid should be eliminated by evaporation.*
4. If the substance is insoluble in the above solvent, try to dissolve in dil.  $HNO_3$  and if it is insoluble in dil.  $HNO_3$ , then try to dissolve in conc.  $HNO_3$ . If conc.  $HNO_3$  also fails to dissolve, then use Aqua regia to dissolve the mixture and filter. Treat the residue separately by special methods. When solution is formed in  $HNO_3$ , heat the filtrate near to dryness and add distilled water and again heat the solution to dryness. Heating to dryness should be repeated two or three times to remove the acid completely. Same procedure is adopted for aqua regia.
5. If the mixture is soluble in conc. HCl and gives white ppt. on dilution which dissolves by adding HCl, Sb, Bi or Sn may be present.
6. If a light yellow ppt appears when solution is formed in dil. HCl, it may be sulphur from  $S_2O_3^{2-}$  which can be removed by heating with  $NH_4NO_3$  and filtering.

#### Solubility Rules

1. All nitrites and nitrates [except  $Hg(NO_3)_2$ ,  $Bi(NO_3)_3$ ], all acetates [except  $Cu(CH_3COO)_2$ ], all chlorides, bromides and iodides [except of  $Ag$ ,  $Hg_2^{2+}$ ,  $Pb^{2+}$ ,  $Cu^+$ ] are soluble in water.  $BiCl_3$  and  $SbCl_3$  and form insoluble oxychlorides in excess of water.
2. All chlorides are soluble except  $AgCl$ ,  $Hg_2Cl_2$  and  $PbCl_2$ .
3. All sulphates are soluble except  $CaSO_4$ ,  $SrSO_4$ ,  $BaSO_4$ ,  $Hg_2SO_4$ ,  $HgSO_4$ ,  $PbSO_4$ , and  $Ag_2SO_4$ .



4. All carbonates are insoluble except those of the IA elements and  $\text{NH}_4^+$ .
5. All hydroxides are insoluble except those of the IA elements,  $\text{Sr}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$ .  $\text{Ca}(\text{OH})_2$  is slightly insoluble.
6. All sulphides are insoluble except those of the IA and IIA elements and  $\text{NH}_4^+$ .
7. All salts of  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  are soluble in water.

### Classification of basic radicals:

Basic radicals are divided into six groups for the purpose of analysis based on the formation of insoluble precipitates with a particular reagent which is called group reagent, e.g.  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$  and  $\text{Pb}^{2+}$  from insoluble chlorides with dill. HCl. Group reagents, nature of precipitates and radicals of six groups are tabulated in table

Table 3.1: Groups of basic radicals

Group	Group reagent	Radicals	Nature of precipitates
I: Silver group IIA: (Cu- Group)	Dill. HCl $\text{H}_2\text{S} + \text{dill. HCl}$	$\text{Ag}^+$ , $\text{Hg}_2^{2+}$ , $\text{Pb}^{2+}$ $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ $\text{Cd}^{2+}$	$\text{AgCl}$ , $\text{Hg}_2\text{Cl}_2$ , $\text{PbCl}_2$ (white ppt.) $\text{HgS}$ , $\text{PbS}$ , $\text{Bi}_2\text{S}_3$ , $\text{CuS}$ , (black) $\text{CdS}$ (Yellow). Ppt. are insoluble in $(\text{NH}_4)_2\text{S}$ and dill. HCl.
II B: (As-group)	Dill. HCl + $\text{H}_2\text{S}$	$\text{As}^{3+}$ , $\text{Sb}^{3+}$ , $\text{Sn}^{2+}$ , $\text{Sn}^{4+}$	$\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{SnS}_2$ soluble in $(\text{NH}_4)_2\text{S}$ .
III: (Fe- group)	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$	$\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$	$\text{Fe}(\text{OH})_3$ , $\text{Al}(\text{OH})_3$ , $\text{Cr}(\text{OH})_3$ (Insoluble hydroxides)
IV: (Zn- group) V: (Ca-group)	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + \text{H}_2\text{S}$ $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + (\text{NH}_4)_2\text{CO}_3 \text{ Sol.}$	$\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Zn}^{2+}$ $\text{Ba}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Sr}^{2+}$	$\text{NiS}$ , $\text{CoS}$ , $\text{MnS}$ , $\text{ZnS}$ (Insoluble sulphides) $\text{BaCO}_3$ , $\text{CaCO}_3$ , $\text{SrCO}_3$ (Insoluble carbonates)
VI: (Alkali group)	No group reagent.	$\text{Na}^+$ , $\text{K}^+$ , $\text{NH}_4^+$ , $\text{Mg}^{2+}$	Ions are not precipitated in previous groups.

### Scheme for the Separation of Cations into Groups

The general scheme for separation of cations into six groups with brief procedure is given in the table below.

Table: Scheme for the Separation of cations into Groups

Add a few drops of dill. HCl to the cold O.S (if the solution is prepared in dill HCl, skip this step). If a ppt. appears, add more HCl till complete precipitation. Filter.			
White heavy curdy ppt.: $\text{PbCl}_2$ , $\text{AgCl}$ and $\text{Hg}_2\text{Cl}_2$ Analyze as Group I. <i>Note: Dirty white or yellow ppt is due to sulphur. Discard it and proceed to the next group.</i>	Filtrate: Acidify the filtrate with HCl and pass $\text{H}_2\text{S}$ till the complete precipitation. Warm and filter. Dilute the filtrate; if a further ppt. is produced pass more $\text{H}_2\text{S}$ and filter. (If the ppt. is light yellow or white, it is due to sulphur by oxidation of $\text{H}_2\text{S}$ , discard).		
	Precipitate: Yellow: $\text{HgS}$ , $\text{CdS}$ , $\text{As}_2\text{S}_3$ Black: $\text{PbS}$ , $\text{CuS}$ Dark brown: $\text{Bi}_2\text{S}_3$ , $\text{SnS}$ Orange: $\text{Sb}_2\text{S}_3$ Dull yellow: $\text{SnS}_2$ Group II	Filtrate: Boil off $\text{H}_2\text{S}$ . If the filtrate is coloured add a few drops of conc. $\text{HNO}_3$ and boil. add solid $\text{NH}_4\text{Cl}_{(s)}$ and boil again, cool and add $\text{NH}_4\text{OH}$ in slight excess Boil and filter while till hot.	
	Precipitate : Gelatinous white: $\text{Al}(\text{OH})_3$ Reddish brown: $\text{Fe}(\text{OH})_3$ Dirty green: $\text{Cr}(\text{OH})_3$ Analyze as Group III.	Filtrate: Pass $\text{H}_2\text{S}$ directly through the alkaline solution and filter.	
		Precipitate: White or grey: $\text{ZnS}$ Flesh coloured: $\text{MnS}$ Black: $\text{CoS}$ Black: $\text{NiS}$ Analyze as Group IV <i>Note: If the original salt is colourless and gives black Ppt. it cannot be of Group IV. Discard and repeat with clean tubes.</i>	Filtrate. Concentrate it to about 10 mL and add a few drops of $\text{NH}_4\text{OH}$ solution and then $(\text{NH}_4)_2\text{CO}_3$ solution in excess. Warm and filter.
		Precipitate: White: $\text{BaCO}_3$ , $\text{CaCO}_3$ , $\text{SrCO}_3$ Analyze as Group V	Filtrate May Contain. $\text{Mg}^{2+}$ , $\text{NH}_4^+$ , $\text{K}^+$ or $\text{Na}^+$ . Analyze as Group VI



### Notes and Explanation

Following precautions must be taken while separating the cations into groups.

1. Small quantity of the salt should be used because it is convenient to handle the small quantity of ppt.
2. Avoid the use of excess amount of reagent as it would lead to wrong conclusions.
3. Always precipitate the group cations completely before proceeding to the next group otherwise the cations of the preceding groups may interfere with cations of the succeeding groups.
4. Wash the precipitate thoroughly to prevent contamination.
5. You may concentrate the solution if it seems to be large quantity

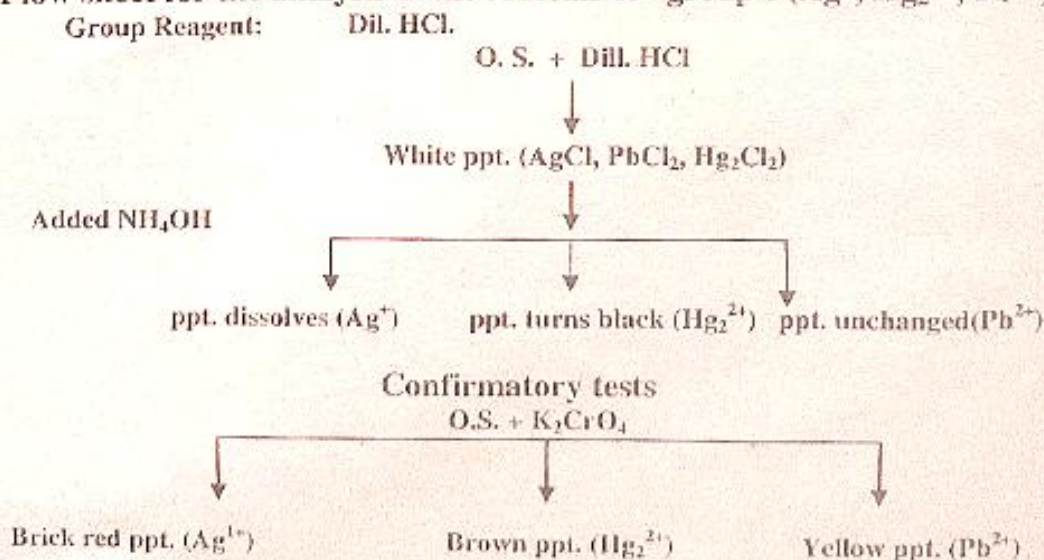
### Analysis of Cations of Group I

**Procedure:** Add dil. HCl to O.S and shake well. Filter and wash the ppt. first with very dilute HCl and then with cold water. Preserve the filtrate for the next group.  
Place the ppt. in a test tube, boil with 10- 15 mL water and filter.

Table 1: Analysis of Group I

<p><b>Filtrate (A)</b>– May contain <math>PbCl_2</math>. Divide the filtrate into two portions.</p> <ol style="list-style-type: none"> <li>1. Cool one portion of the solution under tap water. white ppt. <math>Pb^{2+}</math> indicated</li> <li>2. Add a few drops of <math>K_2CrO_4</math> to a hot portion of the solution. Yellow ppt. soluble in <math>NaOH</math>. <math>Pb^{2+}</math> present</li> <li>3. Add KI solution yellow ppt. of <math>PbI_2</math>. <math>Pb^{2+}</math> confirmed.</li> </ol> <p><b>Lead, <math>Pb^{2+}</math></b></p>	<p><b>Residue:</b> Wash it thoroughly with boiling water and transfer it to test tube. Add <math>NH_4OH</math> Solution to the ppt, Warm and filter.</p> <p><b>Filtrate(B):</b> May contain <math>[Ag(NH_3)_2]Cl</math> Divide the filtrate into parts.</p> <ol style="list-style-type: none"> <li>1. Acidify one portion with dil. <math>HNO_3</math>. White curdy ppt. changing to purple on exposure to light. <math>Ag^+</math> indicated</li> <li>2. To a second portion add KI solution; yellow ppt. insoluble in ammonia. <math>Ag^+</math> indicated</li> </ol> <p><b>Silver, <math>Ag^+</math></b></p>	<p><b>Black residue –Hg (ous):</b> Add 5 drops of conc. <math>HNO_3</math> and 15 drops of conc. HCl and heat to dryness. Dissolve the residue in water to form solution (C).</p> <ol style="list-style-type: none"> <li>1. Dilute one portion with water and pass <math>H_2S</math>; black ppt. <math>HgS</math> indicated</li> <li>2. To solution add solution of <math>SnCl_2</math>. White or grey ppt. <math>Hg_2^{2+}</math> indicated</li> </ol> <p><b>Mercury, <math>Hg_2^{2+}</math></b></p>
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Flow sheet for the analysis of the radicals of group-I ( $Ag^+$ ,  $Hg_2^{2+}$ ,  $Pb^{2+}$ )





## Confirmatory tests for Lead ( $\text{Pb}^{2+}$ ), Silver ( $\text{Ag}^+$ ) and Mercury ( $\text{Hg}_2^{2+}$ )

### Lead ( $\text{Pb}^{2+}$ )

Experiment	Observations	Inference
1. A portion of filtrate (A) + dil $\text{H}_2\text{SO}_4$	White ppt. soluble in ammonium sulphate	$\text{Pb}^{2+}$ confirmed
2. Apply Charcoal cavity test	White malleable bead which marks the paper	$\text{Pb}^{2+}$ confirmed

### Silver ( $\text{Ag}^+$ )

Experiment	Observations	Inference
1. A portion of filtrate (B) + $\text{K}_2\text{CrO}_4$	Red ppt. of $\text{Ag}_2\text{CrO}_4$	$\text{Ag}^+$ confirmed
2. Apply Charcoal cavity test	White silvery bead which does not mark the paper	$\text{Ag}^+$ confirmed

### Mercury ( $\text{Hg}_2^{2+}$ )

Experiment	Observations	Inference
1. Neutral solution (C) + KI	Orange red ppt. of $\text{Hg}_2\text{I}_2$ soluble in excess of KI	$\text{Hg}_2^{2+}$ confirmed
2. Apply Charcoal cavity test	Bright metallic sublimate of Hg droplets	$\text{Hg}_2^{2+}$ confirmed

### Precautionary Notes:

1. Avoid the use of HCl in excess to precipitate the  $\text{PbCl}_2$ ,  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$  because these are soluble in excess of HCl due to complex formation.
2. Wash the ppt. thoroughly with water containing few drops of HCl before separation to remove the adhering solution. This will prevent precipitation of  $\text{BiOCl}$  and  $\text{SbOCl}$ .
3. Very dilute solution of Bi and Sb form white ppt on addition of dil. HCl. These ppt dissolve on addition of more HCl. These should not be confused with  $\text{PbCl}_2$ ,  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ .
4. Aq. solution of thiosulphate also give white or light yellow ppt when dil HCl is added. Ppt pass through filter which can be made soluble by boiling with  $\text{NH}_4\text{NO}_3$  and filtering.
5. Concentrated solution of  $\text{BaCl}_2$  or  $\text{NaCl}$  may also give white ppt on addition of dil HCl due to common ion effect; ppt. dissolves in water.

## Analysis of cations of Group II

Group II comprises of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$  cations which are precipitated as sulphides. Sulphides of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  are insoluble in yellow ammonium sulphide and are grouped as IIA while sulphides of  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$  are soluble in yellow ammonium sulphides and are grouped as IIB.

### Precautions before precipitation of Group II.

- a. Make sure that cations of Group I has been removed completely. Test a small portion of filtrate by adding dil HCl.
- b. Filtrate should not be too acidic because metals such as Cd, Sb and Pb do not precipitate completely in presence of large excess of  $\text{H}^+$  ions. Neutralize the filtrate with  $\text{NH}_4\text{OH}$  and acidify with dil HCl.
- c. Pass  $\text{H}_2\text{S}$  gas through a small portion of filtrate, if coloured ppt are formed then pass  $\text{H}_2\text{S}$  gas through the whole filtrate otherwise proceed to the analysis of Group III.

**Procedure:** Pass  $\text{H}_2\text{S}$  gas through filtrate from Group I, boil it and pass more  $\text{H}_2\text{S}$ , dilute the solution and pass  $\text{H}_2\text{S}$  again until precipitation is complete. Filter and test the few drops of filtrate with  $\text{H}_2\text{S}$ . Preserve the filtrate for the next group.



Ppt. may consist of  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  (Group IIA) and  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Sn}^{4+}$  (Group IIB). Wash the ppt. with dil. Aq. solution of  $\text{H}_2\text{S}$  and transfer the ppt. to a test tube and add yellow ammonium sulphide. Warm the test tube gently and filter.

Residue- May contain sulphides of $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ (Group IIA)	Filtrate. May contain sulphides of $\text{As}^{3+}$ , $\text{Sb}^{3+}$ , $\text{Sn}^{2+}$ , $\text{Sn}^{4+}$ (Group IIB).
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### Confirmatory tests for $\text{Hg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ (Group IIA)

Residue of II-A. Wash the ppt. with dil. Aq. solution of yellow ammonium solution and reject the washing. Transfer the ppt. to a dish, 15 mL dil  $\text{HNO}_3$  and boil for 2-3 minutes. Filter.

Table II A - Analysis of Group II A (Copper Group)

Black residue of $\text{HgS}$ or white residue of $\text{Hg}(\text{NO}_3)_2$ . Dissolve the ppt. in aqua regia (conc. $\text{HCl}$ and $\text{HNO}_3$ 3:1) and dilute. Label it as solution D. 1st portion of D + 3 drops of $\text{SnCl}_2$ solution: White ppt	Filtrate – May contains $\text{Pb}^{2+}$ , $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ . Add about 0.5 mL conc. $\text{H}_2\text{SO}_4$ and heat the solution until dense white fumes evolved. Allow to cool and add few mL water, centrifuge and filter.			
	White ppt. of $\text{PbSO}_4$ . Wash the ppt. and dissolve in few mL of conc. solution of ammonium acetate. Boil the solution and label it as solution E. Portion of E + dil. Acetic acid + $\text{K}_2\text{CrO}_4$ solution $\rightarrow$ yellow ppt. soluble in hot $\text{NaOH}$ solution.	Filtrate – May contain $\text{Bi}^{3+}$ , $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ . Add $\text{NH}_4\text{OH}$ soln. in excess till alkaline. Filter.		Filtrate : May contain complex salts of Cu and Cd, i.e. $[\text{Cu}(\text{NH}_3)_4]^{2+}\text{SO}_4$ (Blue) and $[\text{Cd}(\text{NH}_3)_4]^{2+}\text{SO}_4$ (colourless.) If colourless, Cu, is absent. Pass $\text{H}_2\text{S}$ , a yellow ppt. indicates Cd. If blue, Cu, is present. Label it as solution G.
		White ppt of $\text{Bi}^{3+}$ . Dissolve the ppt. in a minimum quantity of dil. $\text{HCl}$ and label it as F. Solution F + Sod. Stannite solution Black ppt.		
Mercury, $\text{Hg}^{2+}$	Lead, $\text{Pb}^{2+}$	Bismuth, $\text{Bi}^{3+}$	Blue solution Cu present Solution G + acetic acid + $\text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow$ Brown ppt. or colouration.	Solution G + dilute $\text{H}_2\text{SO}_4$ + fine iron fillings or zinc pieces. Boil for few minutes and filter. Neutralize filtrate with ammonia and add a few drops of $\text{HCl}$ and pass $\text{H}_2\text{S}$ ; yellow ppt. of Cds
			Copper, $\text{Cu}^{2+}$	Cadmium, $\text{Cd}^{2+}$

#### Mercury ( $\text{Hg}^{2+}$ )

Experiment	Observations	Inference
1. Solution (D) + $\text{SnCl}_2$	White or grey ppt	$\text{Hg}^{2+}$ confirmed
2. Solution (D) + $\text{NaOH}$	Reddish brown ppt of basic $\text{HgO} \cdot \text{HgCl}_2$	$\text{Hg}^{2+}$ confirmed

#### Lead ( $\text{Pb}^{2+}$ )

Experiment	Observations	Inference
1. A portion of solution (E) + few drops $\text{CH}_3\text{COOH}$ + $\text{K}_2\text{CrO}_4$	Yellow ppt of $\text{PbCrO}_4$	$\text{Pb}^{2+}$ confirmed
2. A portion of solution (E) + dil. $\text{H}_2\text{SO}_4$	White ppt	$\text{Pb}^{2+}$ confirmed

#### Bismuth ( $\text{Bi}^{3+}$ )

Experiment	Observations	Inference
1. A portion of solution (F) + few drops $\text{NaOH}$	White ppt	$\text{Bi}^{3+}$ confirmed
2. A portion of solution (F) + Large excess of water	White ppt. or turbidity of $\text{BiOCl}$	$\text{Bi}^{3+}$ confirmed



Copper ( $\text{Cu}^{2+}$ )

Experiment	Observations	Inference
1. A portion of blue solution (G)+ few drops KI	Reddish brown ppt	$\text{Cu}^{2+}$ confirmed
2. A portion of blue solution (G)+ few drops $\text{CH}_3\text{COOH}$ + 1-2 drops potassium ferrocyanide solution	Reddish brown ppt., the ppt dissolved in $\text{NH}_4\text{OH}$ to give blue solution.	$\text{Cu}^{2+}$ confirmed
3. A portion of blue solution (G)+ few drops $\text{CH}_3\text{COOH}$ + 1-2 drops of NaOH	Blue ppt. which turn black on boiling.	$\text{Cu}^{2+}$ confirmed

## Analysis of cations of Group IIB

Filtrate, i. e the solution in yellow ammonium sulphide: Acidify it with dil. HCl with constant stirring (test with litmus) and pass  $\text{H}_2\text{S}$ . A coloured ppt. shows the presence of As, Sb, Sn, [A fine white or yellow ppt. is of sulphur only. Dissolve it in benzene or  $\text{CS}_2$ . If it dissolve, S is confirmed reject the ppt.] Filter and wash the ppt. with  $\text{NH}_4\text{Cl}$  solution and hot water discard the washings. Boil the ppt. with conc. HCl for 2-3 minutes, dilute with 2-4 mL water. Filter.

Table II B. Analysis of Group II B. (Arsenic Group)

Yellow residue: $\text{As}_2\text{S}_3$ Dissolve it in conc. $\text{HNO}_3$ and label solution as A. Solution A + ammonium molybdate solution & boil yellow ppt. soluble in caustic soda.	Filtrate: Add $\text{NH}_4\text{OH}$ solution to neutralize or just alkaline. Adds solid oxalic acid in excess, boil and pass $\text{H}_2\text{S}$ . Filter.	
Arsenic, $\text{As}^{3+}$	Orange ppt.: $\text{Sb}_2\text{S}_3$ Dissolve the ppt. in smallest amount of conc. HCl label As B. Dilute one portion of solution B with large quantity of water. White ppt. of $\text{SbOCl}$ soluble in HCl.	Filtrate-Boil off $\text{H}_2\text{S}$ . Add a piece of granulated Zn, and dil. HCl. and heat for 3-5 minutes. Label the solution as C. Solution C + $\text{HgCl}_2$ solution $\rightarrow$ a white ppt.
	Antimony, $\text{Sb}^{3+}$	Tin, $\text{Sn}^{2+}$

Confirmatory tests for Arsenic ( $\text{As}^{3+}$ ), Antimony ( $\text{Sb}^{3+}$ ), Tin ( $\text{Sn}^{2+}$ )Arsenic ( $\text{As}^{3+}$  or  $\text{As}^{5+}$ )

Experiment	Observations	Inference
1. A portion of solution (A)+ few drops $\text{NH}_4\text{OH}$ + 0.1 g $\text{NH}_4\text{Cl}$ + $\text{MgSO}_4$ and stir	White ppt. of $\text{MgNH}_4\text{ASO}_4$	$\text{As}^{3+}$ or $\text{As}^{5+}$ confirmed
2. Neutral solution (A) + few drops $\text{CH}_3\text{COONH}_4$ + 1-2 drops $\text{AgNO}_3$	A brownish red ppt. of $\text{Ag}_3\text{AsO}_4$	$\text{As}^{3+}$ or $\text{As}^{5+}$ confirmed

Antimony ( $\text{Sb}^{3+}$ )

Experiment	Observations	Inference
1. A portion of solution (B)+ Pass $\text{H}_2\text{S}$ gas	Orange red ppt of $\text{Sb}_2\text{S}_3$	$\text{Sb}^{3+}$ confirmed
2. Solution (A) + few drops NaOH	White ppt of $\text{Sb}_4\text{O}_6 \cdot x\text{H}_2\text{O}$ soluble in excess of NaOH	$\text{Sb}^{3+}$ confirmed



### Tin ( $\text{Sn}^{2+}$ )

Experiment	Observations	Inference
1. Run ammonium molybdate solution to a portion of solution (C)	Intense blue colour	$\text{Sn}^{2+}$ confirmed
2. Solution (C) + few drops NaOH	White ppt of $\text{Sn}(\text{OH})_2$ soluble in excess of NaOH	$\text{Sn}^{2+}$ confirmed

### Precautionary Notes for Analysis of Group II

1. Sulphides of Group II should not be heated with 50%  $\text{HNO}_3$  for more than 2-3 minutes because  $\text{HNO}_3$  will become concentrated and prolonged heating and concentrated  $\text{HNO}_3$  may convert  $\text{PbS}$  into  $\text{PbSO}_4$  which will remain with  $\text{HgS}$ .
2. Sulphides of Group II should not be heated with yellow ammonium sulphide for more than 5 minutes because  $\text{CuS}$  and  $\text{HgS}$  are slightly soluble in yellow ammonium sulphide and solubility may increase on prolonged heating.

### Detection and Elimination of Interfering Radicals

Addition of  $\text{NH}_4\text{OH}$  to the solution of mixture in presence of certain acid radicals such as tartarate, oxalates, borates, phosphate, fluoride, dichromate and silicate will precipitate not only cations of Group III but also cations of the Groups, IV, V and VI. These acid radicals are called interfering radicals and must be detected and eliminated before proceeding for the analysis of Group III and subsequent groups.

N.B: Students of B.Sc/BS are generally expected to analyze the mixture containing tartarate, oxalate and phosphate only.

#### Detection of Interfering Radicals

Experiments	Observations	Inferences
Solid mixture + Conc. $\text{H}_2\text{SO}_4 \xrightarrow{\text{Heat}}$	Charring occurs	Tartarate present
Solution + $\text{CaCl}_2$	White ppt. soluble in acetic acid	Tartarate present
Solution + $\text{CaCl}_2$	White ppt. insoluble in acetic acid	Oxalate present
Solution + $\text{KMnO}_4$	Colour of $\text{KMnO}_4$ discharged	Oxalate present
Solution + $\text{HNO}_3$ + Ammonium molybdate solution $\xrightarrow{\text{Boil}}$	A yellow crystalline ppt. appears	Phosphate present
$\text{Na}_2\text{CO}_3$ -extract + dil. $\text{HCl} \xrightarrow{\text{Heat}}$ + Zirconyl nitrate reagent	A white gelatinous ppt.	Phosphate present

#### Elimination of Interfering Radicals

1. **Elimination of oxalate, tartarate, citrate and fluoride:** Take about 20 mL of filtrate from Group II in a china dish and add 10 mL cons.  $\text{HNO}_3$ . Heat the mixture to dryness (in fuming hood). Now add 5 mL of conc  $\text{HCl}$  and 5 mL of conc.  $\text{HNO}_3$  to the residue. Evaporate the solution to 2 mL and dilute with 5 mL of water and proceed with the precipitation of Group III and subsequent analysis.
2. **Elimination of Phosphate:**
  - a. Take about 3-5 drops of filtrate from Group II in a test tube and add  $\text{NH}_4\text{OH}$  in excess.
  - b. If no ppt. forms, Cations of Group III, IV, V and Mg are absent. Analyze directly Group VI.
  - c. If ppt. appears, take fresh 3-5 drops of filtrate from Group II in a test tube and add to it a mixture (1:1) of potassium ferricyanide and potassium ferrocyanide. If blue ppt. or colouration appears, iron is present.
  - d. If iron is present take whole of the filtrate from Group II in a beaker, add 2 mL  $\text{HNO}_3$  and boil it for complete oxidation of  $\text{Fe}^{2+}$ . If iron is absent skip this step.



- Add 1-2 g solid  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  to solution from (d) with constant stirring until a slight turbidity appears. Add about 1-2 mL acetic acid and 5-10 mL of conc. ammonium acetate solution or about 3-4 g solid ammonium acetate. Shake well and boil for 2-3 minutes and centrifuge. Preserve the centrifugate for analysis of group IV, V and VI.
- The centrifuge contains  $\text{FePO}_4$ ,  $\text{AlPO}_4$ ,  $\text{CrPO}_4$  and analyze them according to scheme of Group III.
- Add dil.  $\text{NH}_4\text{OH}$  to the reddish centrifugate of step (e) until reddish brown ppt. appears. Add  $\text{NH}_4\text{OH}$  in slight excess, centrifuge and discard ppt. The centrifugate should be free from  $\text{Fe}^{3+}$ .
- Use the centrifugate for analysis of group IV, V and VI.

### Analysis of Group III (Iron Group)

Before proceeding to the analysis of Group III, make sure that:

- Group II has been precipitated completely
- Interfering radicals have been eliminated
- $\text{H}_2\text{S}$  gas has been boiled off completely.

**Procedure:**

- Take filtrate from Group II in a beaker and add about 1 mL conc.  $\text{HNO}_3$  and boil the solution until complete oxidation of ferrous ions. The solution should not give blue colour with  $\text{K}_3[\text{Fe}(\text{CN})_6]$  solution.
- Add about 0.5 g solid  $\text{NH}_4\text{Cl}$  to the above solution and boil to reduce the volume to 1-2 mL.
- Allow to cool the solution and add  $\text{NH}_4\text{OH}$  dropwise with stirring till the smell of ammonia comes out.
- Filter and preserve the filtrate for the analysis of subsequent groups.
- Precipitate may consist of  $\text{Fe}(\text{OH})_3$  - reddish,  $\text{Al}(\text{OH})_3$  - white gelatinous,  $\text{Cr}(\text{OH})_3$  - green.
- Wash the ppt. with 1%  $\text{NH}_4\text{Cl}$  solution and transfer the ppt. to a beaker. Add few mL water, 0.1 g of  $\text{Na}_2\text{O}_2$ , 5 mL 20%  $\text{NaOH}$  solution and 1 mL  $\text{H}_2\text{O}_2$  and boil till evolution of oxygen and filter immediately

Table III A Analysis of Group III (Iron Group)

<b>Reddish brown Residue:</b> Wash the residue with hot water and dissolve it by boiling with dil. $\text{HCl}$ . Label solution as A. Solution A + Potassium thiocyanate $\rightarrow$ blood red colouration. Iron ( $\text{Fe}^{3+}$ ),	Filtrate: If colourless Cr is absent. If yellow, Cr. is indicated. $\text{Al}^{3+}$ is present as soluble $\text{NaAlO}_2$ . If colourless test for $\text{Al}^{3+}$ . If the solution is coloured, acidify with acetic acid and add lead acetate till complete precipitation. Filter	
	<b>Yellow ppt.</b> Dissolve the ppt. in $\text{NaOH}$ and label the solution as B	To this solution add dil. $\text{HCl}$ in slight excess label solution as C
	<b>Chromium (<math>\text{Cr}^{3+}</math>)</b>	<b>Aluminum (<math>\text{Al}^{3+}</math>)</b>

### Confirmatory tests for Iron ( $\text{Fe}^{3+}$ ), Chromium ( $\text{Cr}^{3+}$ ), Aluminum ( $\text{Al}^{3+}$ )

#### Iron ( $\text{Fe}^{3+}$ )

Experiments	Observations	Inferences
Solution A + Ammonium thiocyanate solution	Blood red colour due to formation of $[\text{Fe}(\text{SCN})_6]^{3+}$	$\text{Fe}^{3+}$ confirmed
Solution A + $\text{NaOH}$ solution	Reddish brown ppt of $\text{Fe}(\text{OH})_3$	$\text{Fe}^{3+}$ confirmed

#### Chromium ( $\text{Cr}^{3+}$ )

Experiments	Observations	Inferences
Neutral solution B + dil $\text{HNO}_3$ + $\text{AgNO}_3$ solution	Brick red ppt. of $\text{Ag}_2\text{CrO}_4$	$\text{Cr}^{3+}$ confirmed
Solution B + Few drops of $\text{CH}_3\text{COOH}$ + $\text{BaCl}_2$ solution	Yellow ppt. of $\text{BaCrO}_4$	$\text{Cr}^{3+}$ confirmed

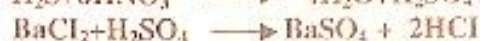


Aluminum ( $\text{Al}^{3+}$ )

Experiments	Observations	Inferences
Few drops of solution C + dil HCl + Litmus solution + $\text{NH}_4\text{OH}$ until alkaline	Blue lake appears	$\text{Al}^{3+}$ confirmed
Solution C + Few drops of dil. $\text{CH}_3\text{COOH}$ + $\text{CH}_3\text{COONa} \xrightarrow{\text{Boil}}$	White ppt.	$\text{Al}^{3+}$ confirmed

## Notes and Explanations

1. Be careful, if lead and Sn(ous) have not been completely removed in the II Group, they will give test for Al.
2. Mn sometimes gets precipitated in the III Group as  $\text{Mn}(\text{OH})_2$  and hence may not be confused with iron.
3. When the interfering acids have not been completely removed, a white ppt. may be obtained in this group, which may be mistaken for Al. This can be avoided by testing the NaOH extract with  $\text{NH}_4\text{Cl}$ -white ppt. indicates Al.
4. Iron comes in the filtrate from Group II in the ferrous form, even if it is present as ferric form, because  $\text{H}_2\text{S}$  reduces it. So it must be oxidized to ferric state before its precipitation, as ferrous hydroxide partially soluble in presence of  $\text{NH}_4\text{Cl}$ .
5. Before the oxidation of ferrous to ferric state with conc.  $\text{HNO}_3$ ,  $\text{H}_2\text{S}$  must be completely boiled off otherwise it will also be oxidized to  $\text{H}_2\text{SO}_4$  and if the original substance contains Ba or Sr, they will be precipitated with this  $\text{H}_2\text{SO}_4$  in the III Group.



## Analysis of Group IV (Zinc Group)

Cations of Group IV are precipitated as sulphides ( $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{MnS}$  and  $\text{ZnS}$ ) in alkaline medium by passing  $\text{H}_2\text{S}$  through their solution.

Procedure: Add  $\text{NH}_4\text{OH}$  in excess to the filtrate from Group III and then add  $\text{NH}_4\text{Cl}$ . Boil and cool and again add few drops of  $\text{NH}_4\text{OH}$  to the solution. Pass  $\text{H}_2\text{S}$  gas until complete precipitation and centrifuge or filter. Preserve the filtrate for analysis of Group V and VI.

Wash the ppt. first with 1%  $\text{NH}_4\text{Cl}$  and then with water. The ppt. may consist of  $\text{CoS}$  (Black),  $\text{NiS}$  (Black),  $\text{MnS}$  (Flesh colour) and  $\text{ZnS}$  (White). If ppt. is not black, Co and Ni are absent. Transfer the ppt. to a beaker and add very dil HCl and shake well. Filter

Table IV—Analysis of Group IV (Zinc Group)

Black residue: $\text{CoS}$ and $\text{NiS}$ . Apply the Borax Bead test on small amount of ppt. Blue bead: $\text{Co}^{2+}$ , Brown bead: $\text{Ni}^{2+}$ . Dissolve the ppt. in conc. HCl with few crystals of $\text{KClO}_3$ and evaporate to dryness. Green residue: $\text{Co}^{2+}$ , Yellowish residue: $\text{Ni}^{2+}$ . Dissolve the residue in water and filter if necessary.		Filtrate: $\text{MnCl}_2$ and $\text{ZnCl}_2$ . Boil off $\text{H}_2\text{S}$ , cool and add excess of NaOH soln. (Test with litmus) and filter.	
I Part Label this part as A: A part of solution A + $\text{NH}_4\text{OH}$ solution until alkaline + excess of dimethyl glyoxime reagent. Red or deep pink ppt. Nickel ( $\text{Ni}^{2+}$ )	II Part Label this part as B A part of solution B + $\text{NH}_4\text{OH}$ in excess + $\text{NH}_4\text{Cl}$ + $\text{K}_3[\text{Fe}(\text{CN})_6]$ sol. Red colouration.	1. White ppt. (turns brown on filter paper): $\text{Mn}^{2+}$ Dissolve this ppt. in conc. $\text{HNO}_3$ and label as C. Fuse a little of the ppt. with $\text{Na}_2\text{CO}_3$ , NaOH and $\text{KNO}_3$ on mica piece. Green mass.	Filtrate – Pass $\text{H}_2\text{S}$ gas : white ppt. (may be dirty) : $\text{Zn}^{2+}$ Dissolve the ppt. in dil. HCl and label as D. A part of solution D + $\text{K}_4[\text{Fe}(\text{CN})_6]$ White ppt.
	Cobalt ( $\text{Co}^{2+}$ )	Manganese ( $\text{Mn}^{2+}$ )	Zinc ( $\text{Zn}^{2+}$ )



## Confirmatory tests for Cobalt ( $\text{Co}^{2+}$ ), Nickel ( $\text{Ni}^{2+}$ ), Manganese ( $\text{Mn}^{2+}$ ), Zinc ( $\text{Zn}^{2+}$ )

### Cobalt ( $\text{Co}^{2+}$ )

Experiments	Observations	Inference
Neutral solution B + A crystal of $\text{KNO}_3 + \text{CH}_3\text{COOH} \xrightarrow{\text{boil}}$	Yellow ppt	$\text{Co}^{2+}$ confirmed
Solution B + $\text{NH}_4\text{SCN}_{(aq)} + 1\text{ml. amyl alcohol}$	Amyl alcohol becomes blue	$\text{Co}^{2+}$ confirmed
A part of solution B + $\text{NH}_4\text{OH}$ in excess + $\text{NH}_4\text{Cl} + \text{K}_3[\text{Fe}(\text{CN})_6]$	A deep red colour	$\text{Co}^{2+}$ confirmed

### Nickel ( $\text{Ni}^{2+}$ )

Experiments	Observations	Inference
A part of solution A + $\text{NH}_4\text{OH}$ solution until alkaline + excess of dimethyl glyoxime reagent	Red or deep pink ppt.	$\text{Ni}^{2+}$ confirmed
Apply Borax Bead Test	Brown bead	$\text{Ni}^{2+}$ confirmed

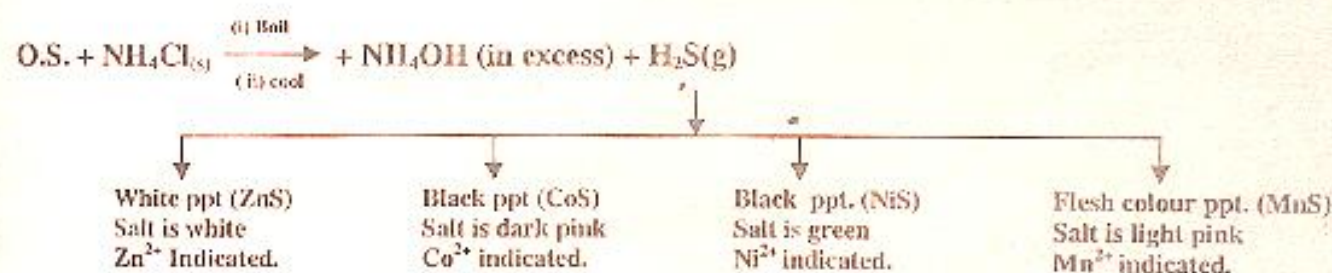
### Manganese ( $\text{Mn}^{2+}$ )

Experiments	Observations	Inference
Dilute a part of solution C with water + Red lead ( $\text{Pb}_3\text{O}_4$ ) $\xrightarrow{\text{boil}}$	Purple colour	$\text{Mn}^{2+}$ confirmed
Apply Borax Bead Test	Violet to red bead	$\text{Mn}^{2+}$ confirmed

### Zinc ( $\text{Zn}^{2+}$ )

Experiments	Observations	Inference
Acidified solution D + Potassium ferrocyanide solution	White ppt.	$\text{Zn}^{2+}$ confirmed
Acidified solution D with acetic acid on spot plate + 1 drop of $\text{HgCl}_2$ solution + 1 drop of ammonium thiocyanate solution	Light pink colour	$\text{Zn}^{2+}$ confirmed

## FLOW SHEET FOR ANALYSIS OF GROUP-IV



## Analysis of Group-V (Calcium Group)

Cations of this group are precipitated as insoluble carbonates ( $\text{BaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{CaCO}_3$ ) by ammonium carbonate in presence of ammonium chloride which partially prevent the precipitation of  $\text{Mg}^{2+}$  due to common ion effect.

### Procedure:

- Boil the filtrate from Group IV to expel the  $\text{H}_2\text{S}$  completely.
- Remove colloidal sulphur (if any) by boiling with ammonium nitrate and filtering.
- Evaporate the solution to concentrate and cool.
- Add few crystals of ammonium chloride and  $\text{NH}_4\text{OH}$  until solution is ammoniacal.
- Add to this solution freshly prepared saturated solution of ammonium carbonate and warm. Cool and filter.
- Wash the ppt. ( $\text{BaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{CaCO}_3$ ) with hot water and dissolve in acetic acid.
- Boil off even traces of  $\text{CO}_2$
- Add  $\text{K}_2\text{CrO}_4$  solution to solution from step (g) and shake well and filter.



Table: Analysis of Group V

Yellow precipitate: $\text{Ba}^{2+}$ Apply flame test: Greasy green flame. Dissolve the ppt. in dil. HCl and label as solution A	Filtrate: Acetates of Sr and Ca. Add conc. solution of ammonium sulphate, boil, cool and filter. White precipitate: $\text{SrSO}_4$ Apply flame test: Crimson flame. Dissolve the ppt. in dil. HCl and label as solution B	Filtrate: $\text{Ca}^{2+}$ To a portion of the filtrate add $\text{NH}_4\text{OH}$ in excess and then ammonium oxalate soln. white ppt. Apply flame test: Orange red flame greenish yellow through blue glass. Calcium, $\text{Ca}^{2+}$
Barium, $\text{Ba}^{2+}$	Strontium, $\text{Sr}^{2+}$	

### Confirmatory Tests for Barium ( $\text{Ba}^{2+}$ ), Strontium ( $\text{Sr}^{2+}$ ), Calcium ( $\text{Ca}^{2+}$ )

#### Barium ( $\text{Ba}^{2+}$ )

Experiments	Observations	Inference
A part of solution A + dil. $\text{H}_2\text{SO}_4$	White ppt.	$\text{Ba}^{2+}$ confirmed
A part of solution A + 1 drop of sodium rhodizonate reagent	A reddish brown ppt	$\text{Ba}^{2+}$ confirmed

#### Strontium ( $\text{Sr}^{2+}$ )

Experiments	Observations	Inference
A part of solution B + $(\text{NH}_4)_2\text{SO}_4$ solution $\rightarrow$ Heat and cool	White ppt.	$\text{Sr}^{2+}$ confirmed
A part of solution B + $\text{KIO}_3$ solution	A ppt. appears	$\text{Sr}^{2+}$ confirmed

#### Calcium ( $\text{Ca}^{2+}$ )

Experiments	Observations	Inference
A part of solution C + $\text{NH}_4\text{OH}$ + Ammonium oxalate solution	White ppt.	$\text{Ca}^{2+}$ confirmed
A part of solution C + 1-2 drops of $\text{K}_4[\text{Fe}(\text{CN})_6]$	Yellow ppt. of $\text{CaK}_2[\text{Fe}(\text{CN})_6]$	$\text{Ca}^{2+}$ confirmed

#### Precautionary Notes:

- If the filtrate from Group IV is brown, it may contain colloidal  $\text{NiS}$ . Add it to acetic acid and boil. Filter and use clear solution for further analysis.
- Use freshly prepared saturated solution of ammonium carbonate solution to precipitate cations of Group V.
- Flame test is the most dependable test for cations of Group V. Perform flame test with solution of cations in conc. HCl

### Analysis of Group VI

There is no group reagent for the cations ( $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ ) of Group VI. Therefore these cations are usually analyzed individually.

#### Procedure:

- Add a few drops of ammonium oxalate solution to the filtrate from Group V.
- Boil, cool and filter. (If cations of group V are absent, skip the step (a) and (b). Discard the ppt., if any, and examine the filtrate for  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{NH}_4^+$ ).
- Add to the filtrate  $(\text{NH}_4)_2\text{HPO}_4$  solutions. Shake vigorously, cool, scratch walls of the test tube with a glass rod and allow standing. Filter.

**Facts about potassium:** Potassium was discovered in 1807 by Sir Humphry Davy, who derived it from caustic potash ( $\text{KOH}$ ). This alkali metal was the first metal that was isolated by electrolysis. There are seventeen isotopes of potassium known to exist.



**Potassium in Diet:** Potassium is a necessary mineral in daily nutrition; it assists in muscle contraction and in maintaining fluid and electrolyte balance in body cells. Potassium is also important in sending nerve impulses as well as releasing energy from protein, fat, and carbohydrates during metabolism. A shortage of potassium can cause a potentially fatal condition known as hypokalemia. Eating a variety of foods that contain potassium is the best way to get an adequate amount. Healthy individuals who eat a balanced diet rarely need supplements. Many fruits, vegetables, and meats contain potassium.

**Precautions:** Solid potassium reacts violently with water. This metal should therefore be kept under a mineral oil such as kerosene.

Table VI : Analysis of Group VI (Sodium group)

<p>White crystalline ppt.: <math>Mg^{2+}</math></p> <p>Filter off ppt. and dissolve it in conc. HCl. Label this solution as A.</p> <p>Solution A + few drops of *Magneson reagent + Excess of NaOH solution: Blue ppt. <math>Mg^{2+}</math> indicated</p> <p>*Magneson reagent is para nitrobenzene azo resorcinol</p>	<p>Filtrate: <math>K^+</math>, <math>Na^+</math> and <math>NH_4^+</math>. Evaporate the solution to dryness in a dish and ignite until white fumes of ammonium salts cease to come out. If no residue is obtained <math>K^+</math> and <math>Na^+</math> are absent. If a residue is obtained add 2-3 mL of water and divided the solution into two portions.</p> <p>Apply flame test to the above residue for <math>Na^+</math> and <math>K^+</math>.</p> <div> <div data-bbox="352 779 699 1317"> <p><b>Part I</b></p> <p>Label this solution as B.</p> <p>Persistent golden yellow flame : <math>Na^+</math></p> <p>Solution B + 1-2 drops of KOH solution + conc. Solution of potassium pyroantimonate + Shake and allow to stand: White crystalline ppt. <math>Na^+</math> indicated.</p> </div> <div data-bbox="715 779 1070 1317"> <p><b>Part II</b></p> <p>Label this solution as C.</p> <p>Violet flame through blue glass: <math>K^+</math>.</p> <p>Solution C + Excess of acetic acid + Freshly prepared solution of sodium cobaltinitrite + alcohol: Yellow crystalline ppt. <math>K^+</math></p> <p>Add acetic acid and <math>Na_3[Co(NO_2)_6]</math> solution to another portion of solution yellow ppt. <math>K^+</math> indicated</p> </div> </div>	<p>Heat the original mixture with NaOH. Solution. Ammonia gas is evolved which gives white fumes with conc. HCl, turns red litmus paper blue and when passed through *Nessler's reagent produces, brown ppt.</p> <p>Dissolve the ammonia gas evolved in water and label the solution as D</p> <ol style="list-style-type: none"> <li>1. To one part add acetic acid in excess and then sodium cobaltinitrite solution; yellow ppt. <math>NH_4^+</math> indicated</li> <li>2. To another portion add Nessler's solution; brown ppt. <math>NH_4^+</math> indicated.</li> </ol>
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### Confirmatory tests for Magnesium ( $Mg^{2+}$ ), Sodium ( $Na^+$ ), Potassium ( $K^+$ ), and Ammonium ( $NH_4^+$ )

#### Magnesium ( $Mg^{2+}$ )

Experiments	Observations	Inference
Apply filter paper ash test	Pink ash.	$Mg^{2+}$ confirmed
A part of solution A + Few crystals of $NH_4Cl$ + 8-Hydroxy quinoline + Few drops of NaOH solution $\xrightarrow{\text{Boil}}$	Yellow ppt.	$Mg^{2+}$ confirmed

#### Sodium ( $Na^+$ )

Experiments	Observations	Inference
A part of solution B + Few drops of KOH solution + Magnesium uranyl acetate reagent	Yellow ppt.	$Na^+$ confirmed
One drop of solution B on a spot plate + one drop of Zinc uranyl acetate reagent & stir	Yellow ppt. or turbidity	$Na^+$ confirmed

#### Potassium ( $K^+$ )

Experiments	Observations	Inference
A part of solution C + Tartaric acid solution + alcohol Shake $\longrightarrow$	White crystalline ppt.	$K^+$ confirmed
A part of solution C + Acetic acid + $Na_3[Co(NO_2)_6]$ solution	Yellow ppt.	$K^+$ confirmed



Ammonium ( $\text{NH}_4^+$ )

Experiments	Observations	Inference
Mix two drops of 5% tannic solution with two drops of 20% $\text{AgNO}_3$ solution and dip a filter paper in this mixture. Place this paper over vapours evolved by heating the aq. extract of the mixture with $\text{NaOH}$	A black stain on paper	$\text{NH}_4^+$ confirmed
A part of solution D + Nessler's reagent + $\text{NaOH}$ solution	Yellow or orange colour	$\text{NH}_4^+$ confirmed

## Precautionary Notes:

1. Concentrate the filtrate from Group V before proceeding to analysis of Group VI
2. Make sure that calcium is absent while precipitating Mg
3. Potassium gives almost all tests of ammonium, therefore, it is necessary to remove every trace of ammonium before testing K.

## Writing of Results of a Mixture Analysis

## (Sample Mixture Analysis)

No	Experiments	Observations	Inference
1	<u>Preliminary Examination of the Mixture</u> i. Noted the colour of the mixture  ii. Heated the dry mixture in a test tube.  iii. Heated the mixture with $\text{NaOH}$ solution. iv. Tested the dry mixture with flame test. v. Applied Filter Ash Test. vi. Applied Charcoal Cavity Test.	Mixture was white amorphous powder.  Smell of ammonia gas was noted. Gas produced white fumes with $\text{HCl}$ . Residue was yellow on heating and white on cooling. Ammonia gas evolved which produced white fumes with $\text{HCl}$ . No Characteristic colored flame. Green ash formed. No bead formed; yellow incrustation in hot which turned white on cooling.	Carbonates, bicarbonates or sulphates of Group IA, IIA or $\text{NH}_4^+$ may be present.  A salt of $\text{NH}_4^+$ and $\text{Zn}^{2+}$ indicated.  $\text{NH}_4^+$ indicated.  $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}$ etc absent. $\text{Zn}^{2+}$ indicated. $\text{Zn}^{2+}$ indicated.
2	<u>Wet Tests for Basic Radicals</u> Preparation of Original Solution (O.S) Solution was prepared in		



i. dil HCl.	No ppt. formed	Basic radicals of first group absent.
ii. O.S + dil. HCl	No ppt. formed	Basic radicals of second group absent.
iii. O.S + dil. HCl + $H_2S$		
<u>Detection of Interfering radicals</u>		
iii. $Na_2CO_3$ -extract + Conc. $H_2SO_4$	No charring occurred	Tartarate absent
iv. $Na_2CO_3$ -extract + $CaCl_2$ sol.	No ppt. formed	Tartarate absent
v. $Na_2CO_3$ -extract + $KMnO_4$ sol.	Colour of $KMnO_4$ did not discharge	Oxalate absent
vi. $Na_2CO_3$ -extract + $(NH_4)_2Mo_7O_{24} \cdot 4H_2O$ sol. $\xrightarrow{\text{Heat}}$	No yellow ppt.	Phosphate absent
vii. Filtrate from Group II was boiled to expel $H_2S$ and $HNO_3$ added $\xrightarrow{\text{Boil and cool}}$ + $NH_4Cl$ $\xrightarrow{\text{Boil and cool}}$ + $NH_4OH$ in excess	No ppt. formed	Radicals of 3 <sup>rd</sup> group absent.
viii. Pass $H_2S$ gas through above solution and filter. Filtrate preserved for next groups.	Ppt. formed.	Radicals of 4 <sup>th</sup> group indicated.
ix. Ppt. was washed with 1% $NH_4Cl$ solution and then water. Noted the colour of ppt.	White ppt.	$Zn^{2+}$ indicated
x. Ppt. dissolved in dil. HCl and $H_2S$ Boiled off. Solution divided into three parts. First part + $NaOH$ sol.	White ppt. soluble in excess of $NaOH$ solution	$Zn^{2+}$ indicated
Second part acidified with acetic acid + Potassium ferrocyanide sol.	White ppt.	$Zn^{2+}$ confirmed.
Third part acidified with acetic acid on a spot plate + one drop of ammoniumthiocyanate sol.	Light pink colour	$Zn^{2+}$ confirmed.



	<p>Filtrate from group 4<sup>th</sup> was heated to expel <math>H_2S</math> gas and concentrated. A few crystals of <math>NH_4Cl</math> and <math>NH_4OH</math> were added to the above solution + Freshly prepared ammonium carbonate sol.</p>	<p>No ppt.</p>	<p>Radicals of 5<sup>th</sup> group absent and 6<sup>th</sup> group indicated.</p>
3	<p>xiv. Above solution was filtered and <math>(NH_4)_2HPO_4</math> sol. added and filtered.</p> <p>xv. Above filtrate was boiled and concentrated. Flame test was applied to residue.</p> <p>xvi. Original mixture was heated in a test tube.</p>	<p>No ppt. formed</p> <p>No Characteristic coloured flame</p> <p>A gas with ammonia smell evolved which produced white fumes with conc. <math>HCl</math>.</p> <p>Brown ppt. formed</p>	<p><math>Mg^{2+}</math> absent</p> <p><math>Na^+</math> and <math>K^+</math> are absent.</p> <p><math>NH_4^+</math> indicated.</p>
	<p>xvii. Ammonia gas was passed into water in a test tube and solution was made. Nessler's Reagent was added to a portion of above solution.</p> <p>xviii. Acetic acid in excess and <math>Na_2[Co(NO_2)_6]</math> sol. was added to another part of the above solution.</p>	<p>Yellow ppt. formed</p>	<p><math>NH_4^+</math> confirmed</p>
4	<p><u>Analysis of acid / radicals</u></p> <p>i. Solid salt + dil. <math>H_2SO_4</math></p> <p>ii. Solid mixture + water</p> <p>iii. Solid salt + Conc. <math>H_2SO_4</math></p>	<p>A colourless and odourless gas evolved with effervescence which turned lime water milky</p> <p>Salt is Insoluble</p> <p>A reddish brown gas which turned Ferrous sulphate paper black</p>	<p><math>NH_4^+</math> confirmed</p> <p>May be <math>CO_3^{2-}</math> or <math>HCO_3^-</math></p> <p><math>CO_3^{2-}</math> indicated and confirmed</p> <p><math>NO_2^-</math> indicated</p>



<p><math>\text{Na}_2\text{CO}_3</math> extract was prepared for wet tests</p> <p>iv. Add few drops of diphenylamine to few drops of sodium extract along the wall of test tube.</p>	<p>A dark blue colour at the junction of two solution.</p>	<p><math>\text{NO}_3^-</math> confirmed</p>
<p>v. To few drops of acidified <math>\text{Na}_2\text{CO}_3</math> extract, few drops of <math>\text{FeSO}_4</math> was added and <math>\text{Conc. H}_2\text{SO}_4</math> was added to this solution along the walls of the test tube.</p>	<p>A brown ring was formed at the junction of the conc. <math>\text{Conc. H}_2\text{SO}_4</math> and <math>\text{FeSO}_4</math>.</p>	<p><math>\text{NO}_3^-</math> confirmed</p>

**Result:** The given mixture contain  $\text{Zn}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$

### Objective questions for practical examination and viva voce

- Q 1. Define salt, radical, acid radical, basic radical, dry tests, wet tests?  
 Ans. Salt is a compound formed by neutralization of an acid by a base, e.g.  $\text{NaCl}$ ,  $\text{KBr}$  etc.  
 An atom or a group of atoms which retains its identity in a chemical reaction is called radical, e.g.,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ .  
 Acid Radical: A radical carrying negative charge is called acid radical e.g.  $\text{Cl}^-$   
 Basic Radical: A radical carrying positive charge is called a basic radical e.g.  $\text{Na}^+$   
 Dry tests: Tests performed with solid salts are called dry tests e.g. flame test.  
 Wet tests: Tests performed with solution of the salt are called wet tests.
- Q 2. Name the radicals of dilute acid group?  
 Ans: Carbonate ( $\text{CO}_3^{2-}$ ), bicarbonate ( $\text{HCO}_3^-$ ), Sulphide ( $\text{S}^{2-}$ ), nitrite ( $\text{NO}_2^-$ ), sulphite ( $\text{SO}_3^{2-}$ ), thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ )
- Q 3. Name the radicals of conc. acid group?  
 Ans. Chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), iodide ( $\text{I}^-$ ), nitrate ( $\text{NO}_3^-$ ), acetate ( $\text{CH}_3\text{COO}^-$ ), oxalate ( $\text{C}_2\text{O}_4^{2-}$ ).
- Q 4. Name the radicals of the special group?      Ans. Sulphate ( $\text{SO}_4^{2-}$ ) and phosphate ( $\text{PO}_4^{3-}$ )
- Q 5. What is charcoal cavity test?      Ans. Already discussed.
- Q 6. What is the function of charcoal in the charcoal cavity test?  
 Ans. Charcoal provides carbon which reduces metal oxides.  

$$\text{PbO} + \text{C} \longrightarrow \text{Pb} + \text{CO}$$
 (White bead)
- Q 7. What is function of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  in the charcoal cavity test?  
 Ans. These act as flux and form the metal carbonates which decompose to form oxides. Metal oxides are reduced to metal by carbon.
- Q 8. What is filter ash test? Give its chemistry?      Ans. Already discussed.
- Q 9. For which radicals filter ash test is performed?      Ans.  $\text{Zn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Sn}^{2+}$  and  $\text{Mg}^{2+}$
- Q 10. Give the colours of ashes formed in filter ash test?  
 Ans. Green ( $\text{Zn}^{2+}$ ), Blue ( $\text{Al}^{3+}$ ), Pink ( $\text{Mg}^{2+}$ ), Dirty bluish green ( $\text{Sn}^{2+}$ )
- Q 11. Give the composition of ashes formed in the filter ash test.  
 Ans. Blue ash (Al) =  $\text{CoO}$ ,  $\text{Al}_2\text{O}_3$ , Pink ash (Mg) =  $\text{CoO}$ ,  $\text{MgO}$ .



Green ash (Zn) = CoO, ZnO, Dirty bluish green (Sn) = CoO, SnO.

- Q12. Describe the chemistry of Borax bead test? Ans. Already discussed.
- Q13. What type of salts give Borax bead test?  
Ans. Coloured salts give Borax bead test.
- Q14. What is formula of Borax? Ans.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$
- Q15. What is the chemical nature of the coloured bead?
- Q16. Coloured beads are of meta borates of the metal under study.
- Q17. What is the function of HCl in flame test?  
Ans. HCl converts metals into metal chlorides which are more volatile than other compounds.
- Q18. Why the platinum wire must be cleaned in flame test?  
Ans. It should be clean because clean wire will not impart any colour to the flame.
- Q19. A compound has a smell of vinegar. Which radical is indicated? Ans.  $\text{CH}_3\text{COO}^-$  (acetate)
- Q20. A solid salt is heated with dill. HCl. Evolution of colourless, odourless gas which turns lime water milky indicates the presence of .....? Ans.  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$
- Q21. What does make lime water milky when  $\text{CO}_2$  is passed through lime water?  
Ans. Lime water becomes milky due to formation of insoluble  $\text{CaCO}_3$   

$$\text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$
- Q22. Name the gas which turns lime water milky? Ans. Carbon dioxide.
- Q23. Write reaction of  $\text{CO}_2$  with lime water.  

$$\text{CO}_2 + \text{Ca(OH)}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$$
- Q24. What does happen when excess of  $\text{CO}_2$  is passed through lime water?  
Ans. Milky colour disappears due to the formation of  $\text{Ca(HCO}_3)_2$  which is soluble in water.  

$$\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{Ca(HCO}_3)_2$$
- Q25. Name two soluble carbonates?  
Ans. Sodium carbonate, potassium carbonate and ammonium carbonate.
- Q26. How will you distinguish between carbonate and bicarbonate?  
Ans. Carbonates form white ppt. with  $\text{BaCl}_2$  solution in cold state, but bicarbonates form white ppt. with  $\text{BaCl}_2$  solution only on heating.
- Q27. Carbonates form white ppt. with  $\text{BaCl}_2$  solution in cold state but bicarbonates form white ppt. with  $\text{BaCl}_2$  solution only on heating why?  
Ans. Carbonate form white ppt. of  $\text{BaCO}_3$  with  $\text{BaCl}_2$  which is insoluble in water but bicarbonates form  $\text{Ba(HCO}_3)_2$  with  $\text{BaCl}_2$ .  $\text{Ba(HCO}_3)_2$  is water soluble.  $\text{Ba(HCO}_3)_2$  forms  $\text{BaCO}_3$  on heating which appears as white ppt.  

$$\text{Ba(HCO}_3)_2 \xrightarrow{\text{Heat}} \underset{\text{(white ppt.)}}{\text{BaCO}_3} + \text{H}_2\text{O} + \text{CO}_2$$
- Q28. A salt is water insoluble. When it is heated with dill. HCl, a colourless gas evolves which turns lime water milky. Which acid radical is indicated? How will you confirm it?  
Ans. Insoluble carbonate is indicated and confirmed.
- Q29. Give one confirmatory test each for  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$   
Ans. Already discussed
- Q30. Give the chemical formulae of the following, lime water, Sodium nitroprusside, Ammonium molybdate, chromyl chloride.  
Ans. Lime water:  $\text{Ca(OH)}_2$ , Sodium nitroprusside:  $\text{Na}_2[\text{Fe(CN)}_5\text{NO}]$   
Ammonium molybdate:  $(\text{NH}_4)_2\text{MoO}_4$ , Chromyl chloride:  $\text{CrO}_2\text{Cl}_2$
- Q31. A compound when reacts with dill.  $\text{H}_2\text{SO}_4$  produces a colourless gas with smell of burning sulphur. Identify the gas and name the radical.  
Ans. A piece of paper dipped in acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is held on the mouth of test tube. It turns green. The gas is  $\text{SO}_2$  which indicates the presence of  $\text{SO}_3^{2-}$ .
- Q32. How will you distinguish between  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_3^{2-}$ ?  
Ans. Both radicals when react with dill.  $\text{H}_2\text{SO}_4$  produce colourless gas with smell of burning sulphur which turns  $\text{K}_2\text{Cr}_2\text{O}_7$  paper green. Note the contents of the test tube. If the contents are yellow, then thiosulphate ( $\text{S}_2\text{O}_3^{2-}$ ) is present. But if no yellow contents, the sulphate is present.
- Q33. What is difference between quick lime and slaked lime?  
Ans. Calcium oxide is quick lime. Quick lime reacts with water to form  $\text{Ca(OH)}_2$  which is called slaked lime.
- Q34. What are the colours of the following gases? Name the corresponding radicals also  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{NO}_2$  and  $\text{HCl}$ ?



Ans.

Gas	Colour	Corresponding radicals
Cl <sub>2</sub>	Yellowish green	Cl <sup>-</sup>
Br <sub>2</sub>	Reddish brown	Br <sup>-</sup>
NO <sub>2</sub>	Brown	NO <sub>2</sub> <sup>-</sup>
I <sub>2</sub>	Violet	I <sup>-</sup>
HCl	Colourless	Cl <sup>-</sup>

- Q35. Can we use conc. HCl instead of conc. H<sub>2</sub>SO<sub>4</sub> in the analysis of conc. acid group?  
 Ans. No. conc acid group contains Cl<sup>-</sup> ion and HCl also has Cl<sup>-</sup> ion. That is why HCl is not used for analysis of conc. acid group.
- Q36. A compound when treated with dill. H<sub>2</sub>SO<sub>4</sub> produce a colourless gas with smell of rotten egg. How will you identify this gas?  
 Ans. If the gas turns lead acetate paper black the gas is H<sub>2</sub>S and it indicates the presence of S<sup>2-</sup>.
- Q37. Give one confirmatory test for S<sup>2-</sup>.  
 Ans. See relevant section.
- Q38. How will you identify S<sup>2-</sup> in a salt?  
 Ans. Salt when treated with dill. HCl produces a colourless gas with smell of rotten egg which turns lead acetate paper black. This indicates the presence of S<sup>2-</sup> in a compound.
- Q39. A compound produces reddish brown gas when treated with dill. H<sub>2</sub>SO<sub>4</sub>? How will you identify the gas?  
 Name it and radical which gives this gas.  
 Ans. The gas is passed onto a piece of filter paper impregnated with FeSO<sub>4</sub> solution. If it turns black, the gas is Nitrogen dioxide (NO<sub>2</sub>) which comes from NO<sub>2</sub><sup>-</sup>.
- Q40. Write one confirmatory test for NO<sub>2</sub><sup>-</sup>.  
 Ans. Already discussed
- Q41. A compound is treated with conc. H<sub>2</sub>SO<sub>4</sub>. It produces a reddish brown gas with pungent smell which indicates the presence of NO<sub>2</sub><sup>-</sup> and Br<sup>-</sup>. How will you distinguish Br<sup>-</sup> from NO<sub>2</sub><sup>-</sup>?  
 Ans. A gas from NO<sub>2</sub><sup>-</sup> (NO<sub>2</sub>) turns ferrous sulphate paper black where as a gas from Br<sup>-</sup> has no effect on the ferrous sulphate paper.
- Q42. What is difference between NO<sub>2</sub> and NO<sub>2</sub><sup>-</sup>?  
 Ans. NO<sub>2</sub> is a brown gas (Nitrogen dioxide) while NO<sub>2</sub><sup>-</sup> is an acid radical.
- Q43. Differentiate between Cl<sup>-</sup>, Cl<sub>2</sub> and Cl.  
 Ans. Cl<sup>-</sup> is an acid radical, Cl<sub>2</sub> is a yellowish gas where as Cl is an atom of chlorine.
- Q44. How will you perform the following tests?  
 Ring Tests, Chromyl chloride Test and Palm Test.
- Ans. **Ring test:**  
 Freshly prepared ferrous sulphate solution is added to 1-2 mL of O.S. of the salt and conc. H<sub>2</sub>SO<sub>4</sub> is poured into the solution along the sides of the test tube. A brown colour ring is formed at the junction.
- Chromyl chloride test**  
 1g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 1g salt (of Cl<sup>-</sup>) is heated with conc. H<sub>2</sub>SO<sub>4</sub> and vapours produced (CrO<sub>2</sub> Cl<sub>2</sub>) are passed into aq. NaOH solution. Lead acetate solution acidified with acetic acid is added to above solution. Yellow ppt. is formed which confirms the presence of Cl<sup>-</sup>.
- $$\begin{array}{lcl}
 \text{NaCl} + \text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 & \longrightarrow & \text{K}_2\text{SO}_4 + 2\text{Na}_2\text{SO}_4 + 2\text{CrO}_2\text{Cl}_2 + 3\text{H}_2\text{O} \\
 \text{CrO}_2\text{Cl}_2 + 2\text{NaOH} & \longrightarrow & \text{Na}_2\text{CrO}_4 + 2\text{HCl} \\
 \text{Na}_2\text{CrO}_4 + \text{Pb}(\text{CH}_3\text{COO})_2 & \longrightarrow & \text{PbCrO}_4 + 2\text{CH}_3\text{COONa} \\
 & & \text{(Yellow ppt.)}
 \end{array}$$
- Palm test**  
 1g oxalic acid, 1g solid salt and 1-2 drops of water are placed on palm and rubbed with thumb on the palm. A smell of vinegar is produced which confirms CH<sub>3</sub>COO<sup>-</sup>.
- $$2\text{CH}_3\text{COONa} + (\text{COOH})_2 \cdot 2\text{H}_2\text{O} \longrightarrow 2\text{CH}_3\text{COOH} + \text{Na}_2\text{C}_2\text{O}_4$$
- Q45. Name the radicals which give the following tests:-  
 (i) Palm test (ii) Ring test (iii) Chromyl chloride test.  
 Ans. (i) CH<sub>3</sub>COO<sup>-</sup> (ii) NO<sub>2</sub><sup>-</sup> (iii) Cl<sup>-</sup>



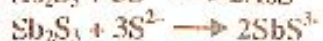
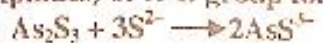
- Q46. Name the compound with formula which is produced when acetate is heated with spirit in the presence of  $\text{H}_2\text{SO}_4$  ?  
 Ans. Ethyl acetate ( $\text{CH}_3\text{COOC}_2\text{H}_5$ )
- Q36. Why is some times heating necessary in conc.  $\text{H}_2\text{SO}_4$  group?  
 Ans. Nitrates of some heavy metals do not evolve  $\text{NO}_2$  when reacted with cold  $\text{H}_2\text{SO}_4$  therefore heating is necessary in these cases.
- Q37. Salt is warmed with conc.  $\text{H}_2\text{SO}_4$  not boiled why?  
 Ans.  $\text{H}_2\text{SO}_4$  is decomposed into  $\text{SO}_2$  and  $\text{SO}_3$  which leads to wrong conclusions.
- Q38. Why is the colour of iodine discharged in confirmatory test of  $\text{S}_2\text{O}_3^{2-}$  radical?  
 Ans.  $\text{I}_2$  is an oxidizing agent and is reduced by  $\text{S}_2\text{O}_3^{2-}$ . So its colour is discharged.  

$$2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$$
(violet) (Colourless)
- Q39. Why the colour of acidified  $\text{KMnO}_4$  is discharged by  $\text{SO}_3^{2-}$ ,  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_2^-$ ?  
 Ans.  $\text{KMnO}_4$  is reduced by the above chemicals into colourless compound.
- Q.40. What are the limitations of the flame test?  
 Ans. The value of the flame test is limited by interference from contaminants that produce brighter colours and by ambiguities where certain different metals cause the same flame colour. Sodium, in particular, is present in many compounds and will colour the flame. Sometimes a coloured glass is used to filter out light from one metal. Cobalt glass is often used to filter out the yellow of sodium.
- Q.41. What is group reagent for group-I of basic radical? Ans. Dil.  $\text{HCl}$ .
- Q42. Name three insoluble chlorides.  
 Ans. Silver chloride, lead chloride and mercurous chloride.
- Q 43. How will you distinguish between bead of Ag and Pb?  
 Ans. White bead of Pb marks the paper while bead of Ag does not mark the paper.
- Q 44. Mercurous ion exist as (a)  $\text{Hg}^+$  (b)  $\text{Hg} - \text{Hg}^{2+}$  (c)  $2\text{Hg}^{1+}$ . Ans. (B)  $\text{Hg} - \text{Hg}^{2+}$  (dimmer)
- Q 45. Why  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  cannot be used as group reagent for group-I of basic radicals?  
 Ans.  $\text{H}_2\text{SO}_4$  is not used because it will precipitate  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  etc in first group.  $\text{HNO}_3$  is not used because nitrites of  $\text{Ag}^{1+}$ ,  $\text{Hg}_2^{2+}$  and  $\text{Pb}^{2+}$  are soluble.
- Q 46. Why charcoal block is used in the charcoal cavity test?  
 Ans. It provides carbon for reducing the metal oxides.
- Q 47. Name three insoluble chlorides? Ans.  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{PbCl}_2$
- Q48. Name the three radicals belonging to 2<sup>nd</sup> group of basic radicals. Ans.  $\text{Cu}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Bi}^{3+}$
- Q49. How are the radicals of group-II precipitated?  
 Ans. These are precipitated as sulphide by passing  $\text{H}_2\text{S}$  gas through O.S. in the presence of dil.  $\text{HCl}$ .
- Q50. What is group reagent for basic radicals of group-II?  
 Ans.  $\text{H}_2\text{S}$  gas in the presence of dil.  $\text{HCl}$ .
- Q51. Write formula of yellow ammonium sulphide, why is it yellow?  
 Ans.  $(\text{NH}_4)_2\text{S}$ . It is yellow due to presence of free sulphur.
- Q52. Why  $\text{Pb}^{2+}$  is placed in I & II group of basic radicals?  
 Ans. Solubility product of  $\text{PbCl}_2$  is greater than those of  $\text{Hg}_2\text{Cl}_2$  and  $\text{AgCl}$ . ( $\text{Hg}_2\text{Cl}_2 = 1.3 \times 10^{-18}$ ,  $\text{AgCl} = 1.8 \times 10^{-10}$ ,  $\text{PbCl}_2 = 2 \times 10^{-5}$ ). Therefore  $\text{Pb}^{2+}$  is not completely precipitated as  $\text{PbCl}_2$ . Moreover  $\text{PbCl}_2$  is slightly soluble in hot water. That is why it is present in I & II group.
- Q53. What are the colours of the following sulphides  $\text{CdS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{PbS}$ , and  $\text{CuS}$ .  
 Ans.  $\text{PbS}$ ,  $\text{CuS}$  = black,  $\text{CdS}$  = Yellow,  $\text{Bi}_2\text{S}_3$  = Black,  $\text{Sb}_2\text{S}_3$  = Orange.
- Q54. How will you distinguish between ppt of  $\text{Hg}^{2+}$  and  $\text{Bi}^{3+}$  in the analysis of II-Group?  
 Ans. ppt. Of  $\text{Bi}_2\text{S}_3$  are soluble in 50%  $\text{HNO}_3$  while  $\text{HgS}$  is insoluble in  $\text{HNO}_3$ .
- Q55. How will you indicate the presence of  $\text{Bi}^{3+}$  in II-group of basic radicals?  
 Ans. ppt. of II-group are dissolved in 50%  $\text{HNO}_3$ ,  $\text{NH}_4\text{OH}$  is added to this solution. Formation of white ppt. Indicates the presence of  $\text{Bi}^{3+}$ .
- Q56. Which statement is true for  $\text{Pb}^{2+}$ ?  
 i)  $\text{PbCl}_2$  is soluble in hot water.  
 ii) Lead is not precipitated in first group  
 iii) Lead does not give charcoal cavity test.  
 iv) Solubility product of  $\text{PbCl}_2$  is greater than other chlorides of Hg and Ag. Ans. (i) and (iv)
- Q58. Give one confirmatory test for  $\text{Cd}^{2+}$ ?  
 Ans. O.S. +  $\text{Na}_2\text{CO}_3$  sol  $\longrightarrow$  white ppt.  $\longrightarrow$   $\text{Cd}^{2+}$  confirmed.



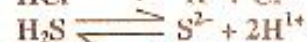
Q59. Why are ppt. of II-B group soluble in yellow ammonium sulphide?

Ans. Ppt. (sulphides) of II-B group form complexes with the  $S^{2-}$  ion which are soluble, e.g.



Q60. Why is added dill. HCl in the O.S. before passing  $H_2S$  gas for the precipitation of II-group of basic radicals?

Ans. HCl is added to prevent precipitation of basic radicals of group (iv) by decreasing the concentration of sulphide ions due to common ion effect.



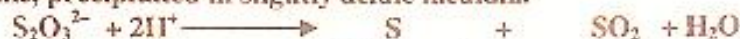
Limited number of  $S^{2-}$  ion are available which can precipitate group-II radicals only.

Q61. Why sulphides of IV group are not precipitated along with group-II by passing  $H_2S$  gas.

Ans. Radicals of group-II are precipitated in the presence of dill. HCl which decreases the ionization of  $H_2S$  due to common ion effect. The solubility product of group-IV sulphides are higher than those of II-group sulphides that is why group-IV sulphides are not precipitated in the presence of dill. HCl.

Q62. Yellow & white ppt. appears some times when  $H_2S$  is passed through O.S. for detection of group-II of basic radicals. why?

Ans. Yellow ppt results from sulphur which is formed by oxidation of  $H_2S$ . The white ppt. is of  $ZnS$  which is some time, precipitated in slightly acidic medium.



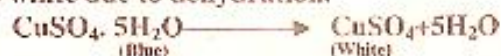
Yellow ppt.



white ppt.

Q63. What happens to copper sulphate, when it is heated?

Ans. It turns white due to dehydration.



Q68. Give one confirmatory test for  $Bi^{3+}$

Ans. O.S + drop of HCl + excess of water  $\longrightarrow$  white ppt.  $Bi^{3+}$  confirmed.

Q69. Name the radicals of group-III of basic radicals?

Ans.  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Fe^{3+}$ .

Q 70. How will you differentiate between  $Fe^{2+}$  and  $Fe^{3+}$ ?

Ans.  $Fe^{3+}$  solution produces blood red ppt. with KSCN but  $Fe^{2+}$  does not.  $Fe^{2+}$  gives green ppt with NaOH but  $Fe^{3+}$  gives red ppt. with NaOH solution. Q 71. What is Lake Test?

Ans. This is confirmatory test for  $Al^{3+}$  Litmus solution along with  $HNO_3$  (1-2 drops) is added to O.S. of  $Al^{3+}$ .  $NH_4OH$  is then added. Blue ppt floats over the colourless solution which confirms  $Al^{3+}$ .

Q 72. Name the group reagent for group-III?

Ans.  $NH_4Cl_{(s)} + NH_4OH$  (excess). (O.S. is boiled with  $HNO_3$  if  $Fe^{2+}$  is indicated).

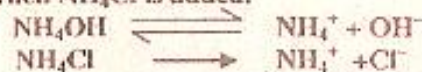
Q 73. Why O.S. of group-III is heated with  $HNO_3$  before adding  $NH_4Cl_{(s)} + NH_4OH$ ?

Ans.  $HNO_3$  is used when salt is light green to oxides  $Fe^{2+}$  into  $Fe^{3+}$ . If  $HNO_3$  is not used  $Fe^{2+}$  form green ppt. with group reagent. Ppt of  $Cr^{3+}$  are also green in group-III. Moreover  $Fe(OH)_2$  is soluble in this medium.

Q 74. What is function of  $NH_4Cl$  and  $NH_4OH$  for the identification of group-III?

Ans.  $NH_4Cl_{(s)}$  is added with  $NH_4OH$  which decreases the ionization of  $NH_4OH$  so that radicals of group-V are not precipitated where as radicals of group-III are precipitated as hydroxide. Decrease in the degree of ionization of  $NH_4OH$  is due to common ion effect.

Solubility products of hydroxides of group-V are higher than those of IIIrd group. Therefore these are not precipitated along with IIIrd group when  $NH_4Cl$  is added.



Q 75. Write the confirmatory tests for  $Cr^{3+}$ ,  $Fe^{3+}$  and  $Al^{3+}$ .

Ans. See respective radical in the note book.

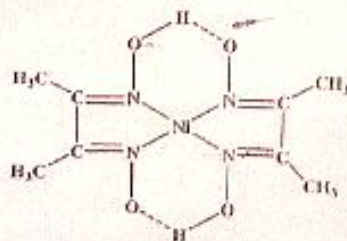
Q 76. What is colour of ferric phosphate? Ans. Yellowish brown.

Q 77. Cations of IIIrd group are precipitated as..... Ans. Hydroxide.

Q78. What is chemical nature (composition) of ash formed in filter ash test of AL. (Ans. It is  $Al_2O_3$ ,  $CoO$ ).



- Q73. Name the radical of IIIrd group which produces a dark blue ppt with  $K_3[Fe(CN)_6]$ ? Ans.  $Fe^{2+}$
- Q74. Name the radical which forms white gelatinous ppt with NaOH solution? Ans.  $Al^{3+}$
- Q75. Give the name of green ppt of IIIrd group which is soluble in excess of NaOH solution to form green solution?  
Ans.  $Cr(OH)_3$
- Q76. Give formulae of (i) Potassium sulphocyanide (ii) Potassium ferricyanide (iii) Potassium ferrocyanide.  
Ans. (i)  $KSCN$  (ii)  $K_3[Fe(CN)_6]$  (iii)  $K_4[Fe(CN)_6]$
- Q77. How will you identify the radicals of 3<sup>rd</sup> group of basic radicals?  
Ans. White gelatinous ppt. of white salt indicates  $Al^{3+}$ , reddish brown ppt. of light green salt indicates  $Fe^{2+}$  and reddish brown ppt. of yellow salt indicates  $Fe^{3+}$ . Dirty green ppt. of green salt indicates  $Cr^{3+}$ .  
Ans. (b).
- Q78. Large excess of  $NH_4OH$  should be avoided to precipitate radicals of group-III, why?  
Ans. Hydroxides of Al and Cr are soluble in excess of  $NH_4OH$  so large excess of  $NH_4OH$  should be avoided.
- Q79. Why,  $NH_4Cl(s)$  is added first and then  $NH_4OH$  to O.S. for the analysis of group-III.  
Ans. If we add  $NH_4OH$  excess, the radical group-IV and V will be precipitated along with radicals of group-III and function of  $NH_4Cl(s)$  is lost.
- Ans. Borax bead test is performed for coloured salts only.
- Q80. What is the colour of bead of  $Ni^{2+}$ ?  
Ans. Reddish brown in oxidizing and grey black in reducing flame.
- Q81. What is the colour of  $Mn^{2+}$  bead in oxidizing and reducing flame?  
Ans. Violet in oxidizing and colourless in the reducing flame.
- Q82. What is group reagent of basic radicals for group IV?  
Ans.  $NH_4Cl(s) + NH_4OH + H_2S$  (gas)
- Q83. Write the colour of  $CoS$ ,  $MnS$ ,  $ZnS$  and  $NiS$   
Ans.  $CoS$ ,  $NiS$  = black,  $MnS$  = Flesh colour,  $ZnS$  = White
- Q84. What is philosopher's wool? Ans.  $ZnO$  is called philosopher's wool.
- Q85. Write formula of dimethylglyoxime?  
Ans.  $CH_3 - C = NOH$
- $$\begin{array}{c} | \\ CH_3 - C = NOH \end{array}$$
- Q86. Give one confirmatory test for  $Ni^{2+}$ . Ans.  $Ni^{2+}$  form rose red ppt with DMG solution.
- Q87. Which radicals of group-IV of basic radicals give Borax Bead Test? Ans.  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Mn^{2+}$
- Q88. Which radical of group IV gives filter ash test? Ans.  $Zn^{2+}$
- Q89. What is function of  $NH_4OH$  in the detection of group IV of basic radicals?  
Ans.  $NH_4OH$  increases the concentration of  $S^{2-}$  from  $H_2S$  so that sulphides of group IV are precipitated easily.
- $$H_2S \rightleftharpoons 2H^+ + S^{2-}$$
- $$\begin{array}{l} NH_4OH \rightleftharpoons NH_4^+ + OH^- \\ OH^- + H^+ \longrightarrow H_2O \end{array}$$
- Q90. How will you confirm the presence of  $Mn^{2+}$ ?  
Ans.  $Na_2HPO_4$  solution is added to O.S. Flesh colour (yellowish - pink) ppt. is formed which confirms the presence of  $Mn^{2+}$ .
- Q91. Write formula of ppt. which is formed by O.S of  $Ni^{2+}$  and DMG sol?  
Ans.



Structure of bis(dimethylglyoximate) Ni (0)

- Q92. O.S. of a salt gives light green ppt. with  $Na_3PO_4$  sol. Name the radical. To which group of basic radical it belongs? Ans.  $Ni^{2+}$ , IVth group
- Q93. Name the radicals of group V of basic radicals? Ans.  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$



- Q94. What is group reagent for group V of basic radicals?  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$  in excess +  $(\text{NH}_4)_2\text{CO}_3$  sol.
- Q95. What is the nature of ppt. of group-V of basic radicals?
- Ans. Ppt. of group-V is carbonates of  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ .
- Q96. What are colours of salts and ppt. of group-V? Ans. Salts and ppt. of group-V are colourless.
- Q97. What is the origin of different colours of flame in flame test?
- Ans. When salts of certain metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  etc.) are heated in the oxidizing flame, electrons of these atoms absorb different radiations emitted by flame and get excited. Excited atoms are unstable and electron return back from excited state to ground state by emitting radiations of different frequencies which fall in the visible region of the spectrum and flame becomes coloured.
- Q98. Why paste of salt is made with HCl. to perform flame test?
- Ans. HCl converts metals to their chlorides which are more volatile and are easily vaporized and colour is easily detected.
- Q99. Why platinum wire is used for performing flame test?
- Ans. Platinum wire does not impart any colour to flame and is chemically inert. Therefore it is used in flame test.
- Q100. How will you differentiate between  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  salts by flame test?
- Ans.  $\text{Ca}^{2+}$  gives brick red flame,  $\text{Ba}^{2+}$  gives apple green flame and  $\text{Sr}^{2+}$  gives crimson colour flame.
- Q102. What is the function of  $\text{NH}_4\text{Cl}$  in the detection of group-V of basic radicals?
- Ans.  $\text{NH}_4\text{Cl}$  suppresses the ionization of  $(\text{NH}_4)_2\text{CO}_3$  so that limited number of  $\text{CO}_3^{2-}$  ions are produced which cannot precipitate  $\text{Mg}^{2+}$  in group-VI.
- Q103. Why  $\text{NH}_4\text{OH}$  is added to O.S of group-V before adding  $(\text{NH}_4)_2\text{CO}_3$ ?
- Ans.  $(\text{NH}_4)_2\text{CO}_3$  also contains  $\text{NH}_4\text{HCO}_3$  which does not form ppt. with the cations of group V. So  $\text{NH}_4\text{OH}$  is added to convert  $\text{NH}_4\text{HCO}_3$  into  $(\text{NH}_4)_2\text{CO}_3$ .



- Q104. Why  $\text{Ca}^{2+}$  is not precipitated sometimes in group-V and passes to filtrate?
- Ans.  $(\text{NH}_4)_2\text{CO}_3$  contains a large percentage of  $\text{NH}_4\text{HCO}_3$  which forms  $\text{Ca}(\text{HCO}_3)_2$  with  $\text{Ca}^{2+}$  which is soluble in water and goes to filtrate. This happens when insufficient  $\text{NH}_4\text{OH}$  is added.
- Q105. Why  $\text{Na}_2\text{CO}_3$  is not used as group reagent for detection of group (V) of basic radicals?
- Ans.  $\text{Na}_2\text{CO}_3$  is not used as group reagent for group (V) because it precipitates  $\text{Mg}^{2+}$  also.
- Q.106 What is difference between an organic and inorganic compound?
- Ans. An organic compound is any member of a large class of chemical compounds whose molecules contain carbon and hydrogen; therefore, carbides, carbonates, carbon oxides and elementary carbon are not organic. Organic compounds have carbon as essential element and are covalent in nature; they are usually of animal or plant in origin; inorganic compounds may consist of any of the elements and are usually ionic in nature.
- Q. 107. What is layer test?
- Ans. This test is performed for the detection of bromide and iodide. Take 2 mL  $\text{Na}_2\text{CO}_3$ -extract and 2 mL chloroform in a test tube, add 2 mL chlorine water and shake well. Formation of brown layer indicates bromide and violet layer indicates iodide.
- Q. 108. What is meant by salt analysis?
- Ans. Detection of acid and basic radical is called salt analysis.
- Q. 109 How will you distinguish between  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ ?
- Ans.  $\text{Sn}^{2+}$  forms dark brown appt. of  $\text{SnS}$  and  $\text{Sn}^{4+}$  forms yellow ppt. of  $\text{SnS}_2$  when solution of salt is treated with HCl and  $\text{H}_2\text{S}$ .
- Q. 110 Why radicals are grouped together?
- Ans. Radicals are grouped together for systematic analysis.
- Q. 111 What is meant by a deliquescent substance?
- Ans. A substance which absorbs moisture is called a deliquescent substance, e.g.  $\text{NaOH}$ ,  $\text{CaCl}_2$ ,  $\text{P}_2\text{O}_5$ .
- Q. 112 What is precipitate?
- Ans. An insoluble substance formed by mixing two solutions is called precipitate.
- Q. 113. A salt when reacted with dil.  $\text{H}_2\text{SO}_4$ , produces colourless gas which turns lime water milky, Name the indicated radicals. Ans.  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ .
- Q. 114. A salt was treated with dil  $\text{H}_2\text{SO}_4$ . A gas of rotten egg produced which turned lead acetate paper black, Which radical of the acid radicals was indicated? (Ans.  $\text{S}^{2-}$ ).
- Q. 115. How will you distinguish between  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ?



Ans. Salt solution of  $\text{CO}_3^{2-}$  produces white ppt, with solution of  $\text{CaCl}_2$  or  $\text{MgSO}_4$  in cold state where as  $\text{HCO}_3^-$  produces white ppt, with salt solution  $\text{CaCl}_2$  or  $\text{MgSO}_4$  on heating.

Q.116. Which radicals give  $\text{SO}_2$  gas when reacted with dil  $\text{H}_2\text{SO}_4$ ?

Ans.  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  give off  $\text{SO}_2$  gas when treated with dil,  $\text{H}_2\text{SO}_4$ .

Q.117. Write down names of insoluble carbonates?

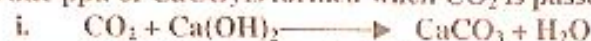
Ans. Magnesium carbonate ( $\text{MgCO}_3$ ) and calcium carbonate ( $\text{CaCO}_3$ ).

Q.118. A salt is water insoluble, when solid salt is treated with dil,  $\text{H}_2\text{SO}_4$ , a colourless gas is produced which turns lime water milky, Salt imparts brick red colour to flame, which acid and basic radicals are indicated?

Ans.  $\text{CO}_3^{2-}$  and  $\text{Ca}^{2+}$

Q.119. Write the chemical reactions which occur when  $\text{CO}_2$  is passed through lime water?

Ans. White ppt. of  $\text{CaCO}_3$  is formed when  $\text{CO}_2$  is passed through limewater.



ii. When  $\text{CO}_2$  is passed after formation of  $\text{CaCO}_3$ ,  $\text{Ca(HCO}_3)_2$  is formed which is soluble.

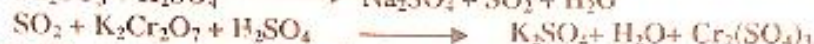


Q.120. Name the radical of the dil, acid group, which produces coloured, gas with dil.  $\text{H}_2\text{SO}_4$ . How will you identify the gas?

Ans.  $\text{NO}_2^-$  produces brown colour gas, which turns ferrous sulphate paper black.

Q.121. Why does the colour of  $\text{K}_2\text{Cr}_2\text{O}_7$  paper become green when it is exposed to gas coming out from  $\text{SO}_3^{2-}$  or  $\text{S}_2\text{O}_3^{2-}$ ?

Ans.  $\text{SO}_3^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  evolve  $\text{SO}_2$  gas when treated with dil,  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_2$  reacts with acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  to form green ppt. of  $\text{Cr}_2(\text{SO}_4)_3$ .

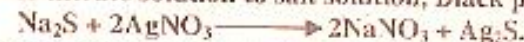


Q.122. Why is  $\text{FeSO}_4$  solution turned black when gas coming out from nitrite is passed through it?

Ans. Nitrites when treated with dil,  $\text{H}_2\text{SO}_4$  produce  $\text{NO}_2$  gas.  $\text{NO}_2$  forms  $\text{FeSO}_4\text{NO}$ , which is black.

Q.123. Write a confirmatory test for  $\text{S}^{2-}$  radical?

Ans. Add silver nitrate solution to salt solution, Black ppt. conforms  $\text{S}^{2-}$ .



Q.124. Write down a confirmatory test for  $\text{SO}_3^{2-}$  radical.

Ans. Add silver nitrate solution to salt solution. Formation of white ppt confirms  $\text{SO}_3^{2-}$

Q.125. What happen when  $\text{NH}_4\text{OH}$  is added to yellow ppt of  $\text{AgI}$ .

Ans. It remains insoluble.

Q.126. What is colour of flame of  $\text{Sr}^{2+}$  salt. Ans. Crimsons red bloods red.

Q.127. An organic compound is heated with \_\_\_\_\_ to detect C and H.

Ans. Copper oxide.

Q.128. Which gas is evolved when  $\text{Br}^-$  salt is heated with conc.  $\text{H}_2\text{SO}_4$ ?

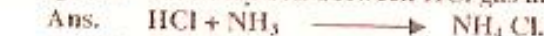
Ans. Bromine gas.

Q.129. What happens when  $\text{NaOH}$  solution is added to  $\text{Mg}^{2+}$  salt solution?

Ans. White ppt. of  $\text{Mg(OH)}_2$  is formed.

Q.130. Name basic radical, which is confirmed by using  $\text{NH}_4\text{OH}$  and diethyl glycoside? Ans.  $\text{Ni}^{2+}$  (Nickel)

Q.135. Give reaction between  $\text{HCl}$  gas and aqueous  $\text{NH}_3$  solution?

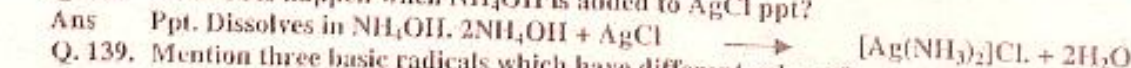


Q.136. Name the gas, which turns  $\text{FeSO}_4$  solution black? Ans.  $\text{NO}_2$

Q.137. What is the group reagent for group-I of basic radicals and why?

Ans. Dil.  $\text{HCl}$  is group reagent for group-I of basic radicals because it forms  $\text{Hg}_2\text{Cl}_2$ ,  $\text{AgCl}$  and  $\text{PbCl}_2$  which are insoluble.

Q.138. What does happen when  $\text{NH}_4\text{OH}$  is added to  $\text{AgCl}$  ppt?



Q.139. Mention three basic radicals which have different colours?

Ans.  $\text{Fe}^{2+}$  = Light green

$\text{Cu}^{2+}$  = Blue

$\text{Ni}^{2+}$  = Bright Light

$\text{Co}^{2+}$  = Pink

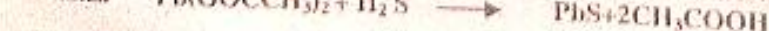
Q.140. Is  $\text{PbS}$  soluble? What its colour? Ans.  $\text{PbS}$  is insoluble in water, its colour is black.

Q.141. Name any basic radical, whose solution gives white ppt. only on adding distilled water in excess?

Ans.  $\text{Bi}^{2+}$

Q.142. Give formula of potassium chromate? Ans.  $\text{K}_2\text{CrO}_4$

Q.143. Give equation of reaction, when  $\text{H}_2\text{S}$  turns lead acetate solution black?





Q.145. Write down equation for reaction of any metal chloride with  $\text{AgNO}_3$ ?

Ans  $\text{NaCl} + \text{AgNO}_3 \longrightarrow \text{AgCl} + \text{NaNO}_3$

Q.146. What is the formula of the brown compound formed in Ring Test for  $\text{NO}_3^{-1}$  radical.

Ans  $[\text{Fe}(\text{NO})]\text{SO}_4$ .

Q.147. What is chemistry of Ring Test?

Ans Ring Test is performed for confirmation of  $\text{NO}_3^{-1}$  radical. Freshly prepared  $\text{FeSO}_4$  is added to solution of the sample and conc.  $\text{H}_2\text{SO}_4$  is added along the sides of test tube, brown ring is formed at the junction of two solutions. Following reactions are involved.



Q.148. Mention a test to distinguish between  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ .

Ans Add  $\text{BaCl}_2$  solution to salt solution. A white ppt soluble in dil.  $\text{HCl}$  indicates  $\text{PO}_4^{3-}$  and white ppt. insoluble in dil.  $\text{HCl}$  indicates  $\text{SO}_4^{2-}$ .

Q.149. What group reagents are used to precipitate basic radicals of group-IV?

Ans To O.S.  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$  are added to precipitated basic radicals of group-IV.

Q.150. Give formula of one coloured potassium salt?

Ans  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ .

Q.151. Mention any two reagents to distinguish between soluble carbonate and bicarbonate.

Ans.  $\text{MgSO}_4$  solution  $\text{BaCl}_2$  solution.

Q.152. Mention all the radicals with valence present in the group to which  $\text{S}^{2-}$  belongs.

Ans  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$ .

Q.153. Write down formula of three soluble carbonates?

Ans  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ .

Q.154. What for Kipp's apparatus is used?

Ans It is used for preparing  $\text{H}_2\text{S}$  gas in the laboratory.

## Volumetric Analysis

### Introduction

The volumetric analysis is a type of quantitative analysis in which volume of a solution taken in burette is measured which is required to react completely with a measured volume of another solution taken in the titration flask. An indicator is used to show the completion of the reaction.

The volumetric analysis is based on:

1. Neutralization reactions
2. Oxidation reduction reactions
3. Precipitations
4. Complexation reactions

Volumetric calculations are based on the molarity equation:

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$M_1$  and  $M_2$  are molarities of the standard and unknown solutions.  $V_1$  and  $V_2$  are the volumes and  $n_1$  and  $n_2$  shows the number of moles of the two substance which react together. These are known from the balanced chemical equation of the reaction.

### 3.1 Basic terminology

1. **Titration:** Titration is defined as the practical process of determination of the strength of unknown solution by allowing it to react with a solution of known strength.
2. **Standard solution:** A solution of known concentration is called standard solution.
3. **Primary standard:** A substance that can be used directly for the preparation of a standard solution without reference to some other concentration is called a primary standard e.g.  $\text{Na}_2\text{CO}_3$ , oxalic acid etc.
4. **Titrant:** The solution taken in the burette is called titrant. Solution of acid and  $\text{KMnO}_4$  are usually titrants.
5. **Titrand:** The solution taken in the titration flask is called titrand or titrates.



6. **Indicator:** Indicator is a chemical compound which reversibly changes its colour depending on the pH of the solution in which it is dissolved. It shows the completion of reaction by change in the colour of the solution in titration flask. For example phenolphthalein and methyl orange are indicators used in acid base titrations.
7. **End point:** The stage in a titration when the indicator undergoes a maximum change in colour due to a small amount of added titrant is called end point. The end point is marked by the change in colour of the indicator. End point shows the completion of the reaction.
8. **Equivalence point:** A stage when stoichiometric amount of one substance reacts with the stoichiometric amount of the other substance during titration is called equivalence point. It is ahead of end point.
9. **Meniscus:** The curved surface of the liquid in a tube of small bore is called meniscus. The upper meniscus of the coloured liquid and lower meniscus of the colourless liquid are noted.
10. **Anti-parallax card or paper:** The piece of paper or card used to remove the error due to parallax is called anti-parallax paper.
11. **Concentration or strength of solution:** A quantity of solute dissolved per ml. of the solution or solvent is called concentration e.g. 0.1 M or 1% of HCl are concentrations of HCl solution.
12. **Molecular weight:** The sum of average relative masses of all the atoms in a molecule is called molecular weight.
13. **Molarity:** It is the number of moles of the solute dissolved per  $\text{dm}^3$  of the solution.

$$\text{Molarity} = \frac{\text{Weight of the solute}}{\text{Molecular weight} \times \text{vol. of solution in dm}^3}$$

14. **Concordant Readings:** The burette readings which do not differ from each other by more than 0.1 are called concordant readings.
15. **Rinsing:** After washing the glass apparatus, the solution to be measured is taken in the burette or pipette and poured off. This is called rinsing.



Figure 3.1(a): How to use stop cork of the burette.

### General Procedure of volumetric analysis

Glass apparatus used in the volumetric analysis should be clean. Wash the burettes, pipettes and conical flasks with chromic acid solution and then with tap water and finally with distilled water. Follow the general procedure for titration as given below.

1. Rinse the burettes and pipettes before use with the solution to be used and rinse the flasks with distilled water.
2. Fix the burette into the burette holder, taking care that it is vertical and stable. Place a

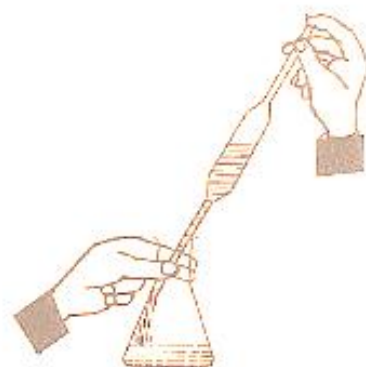
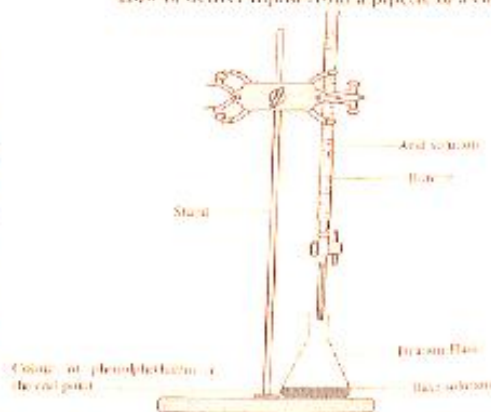


Fig. 4.1

How to deliver liquid from a pipette to a conical flask

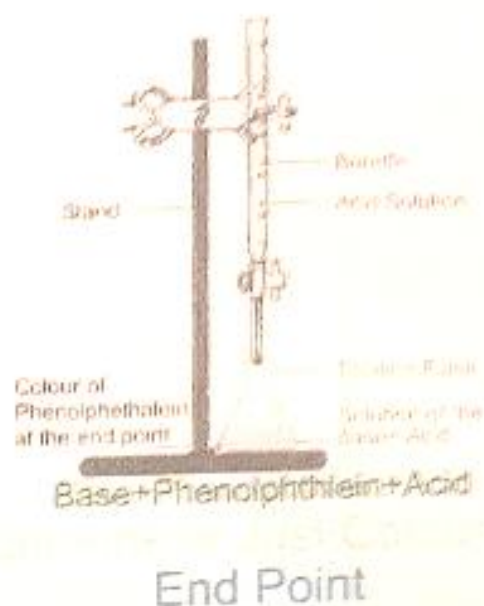
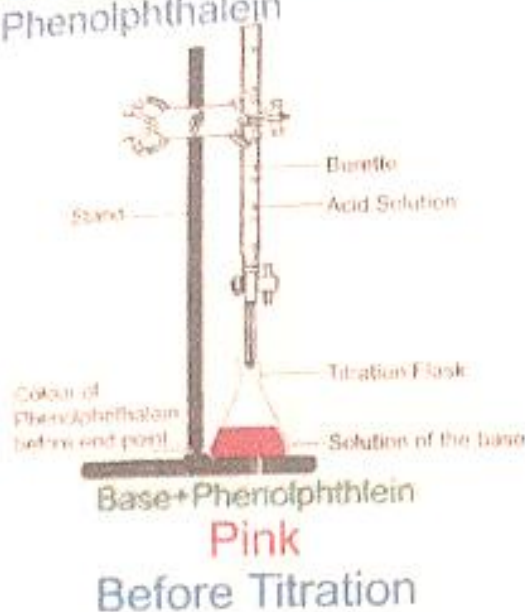




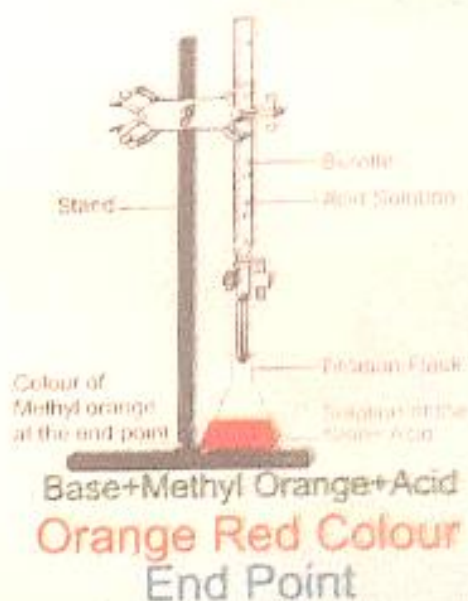
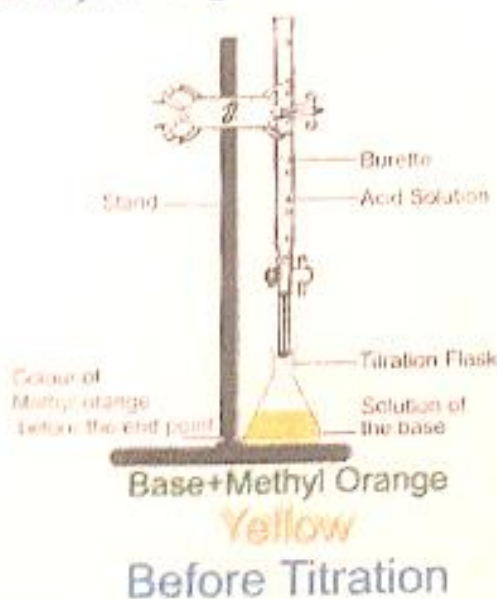
# CHART OF END POINTS IN ACID BASE TITRATIONS

## (a) Acid Base Titrations

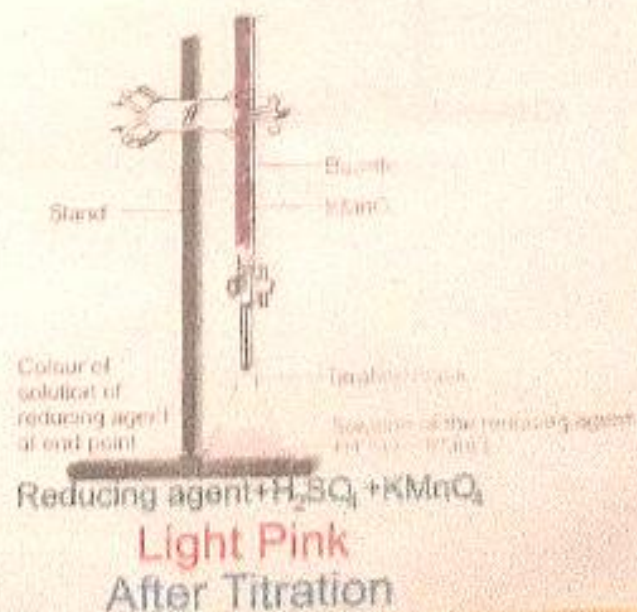
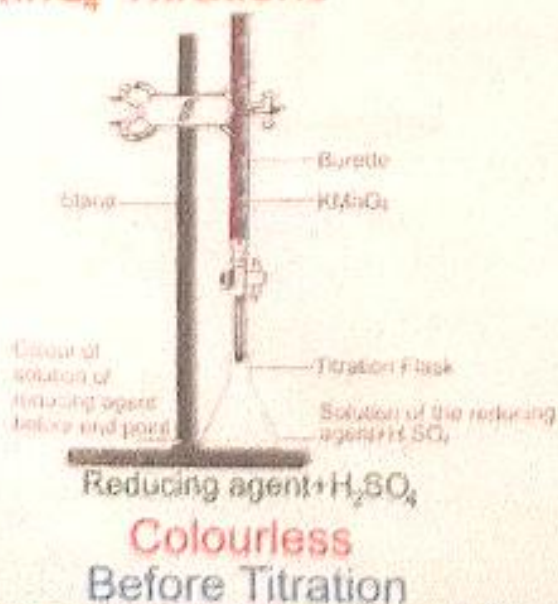
### (i) Phenolphthalein



### (ii) Methyl Orange



## (b) $\text{KMnO}_4$ Titrations

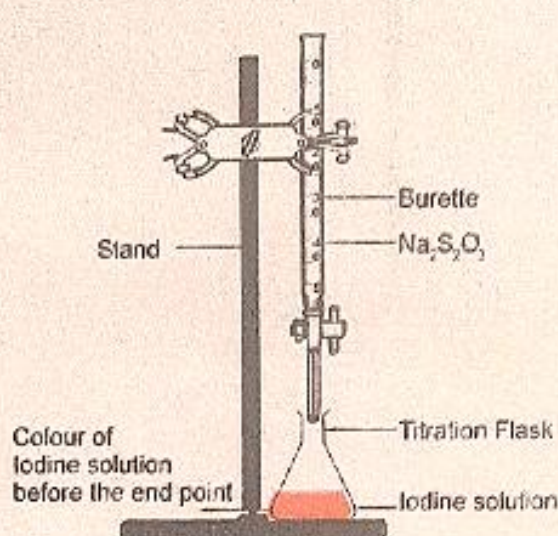




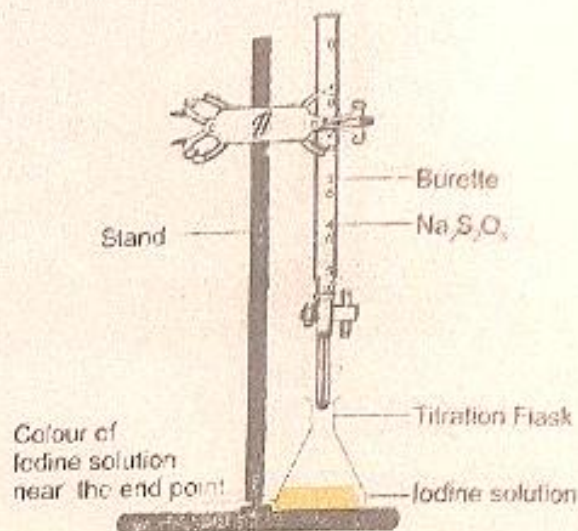
# CHART OF END POINTS IN IODINE TITRATIONS

## Iodine Titrations

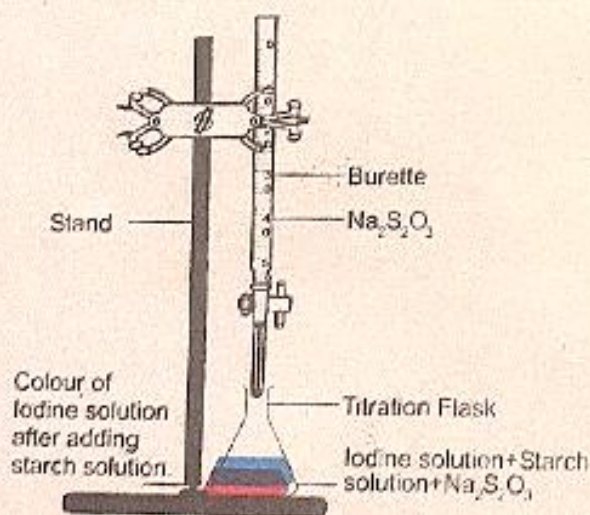
(i) Iodometry (Iodine is liberated from KI by oxidizing agent in the flask)



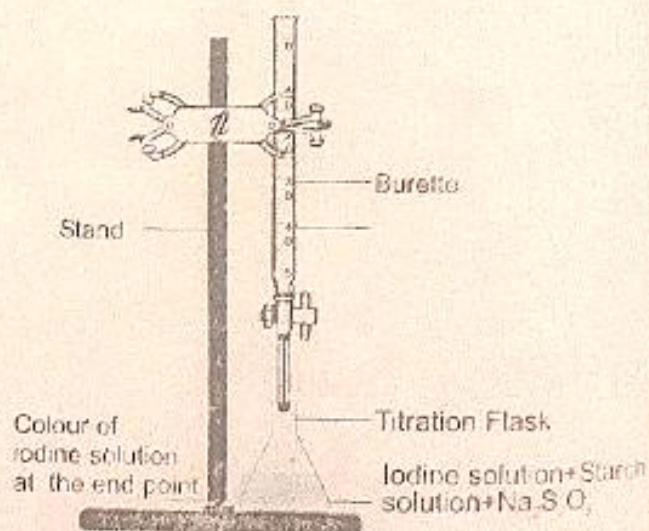
**Dark Brown**  
Before Titration



**Pale Yellow**  
Near End Point



**Intense Blue**  
After adding Starch Sol.



**Just Colourless Very Light Blue**  
End Point

(ii) Iodimetry (Direct Titration of Iodine solution with reducing agents.)

Colour scheme of end point in Iodimetry is same as in Iodometry.



beaker under the burette as shown in figure 3.2. Close the tap, and run some distilled water into the top of the burette. Let the water clean the inside of the burette. Open the tap, and allow the water to drain out. Repeat.

3. Close the tap, and (using the funnel) run some of the required reagent, e.g. acid, into the top of the burette. Open the tap, and allow the reagent to drain through into the beaker. Repeat.
4. Remove the funnel. Make sure that there are no air bubbles inside the burette. *Slowly open the tap, and allow the reagent to run down to (or just past) the 0.0 ml. mark. Close the tap.*
5. Remove the beaker, and place a white tile under the burette. Put a conical flask on the white tile, and adjust the height of the burette so that the tip is just above the lip of the conical flask.
6. Remove any air bubble in the burette or pipette before taking measurement. *Do not blow the pipette to remove the last drop from the pipette but touch it with the bottom of the flask as show in fig.*
7. Solution from the burette should not fall on the walls of the titration flask.
8. Use anti-parallax paper to read the burette reading. Note lower meniscus of colourless solution and the upper meniscus of the coloured solution
9. Acid and  $\text{KMnO}_4$  solutions are always taken in the burette
10. Take the stop cork of the burette in your left hand and swirl the titration flask with right hand. *Do not shake the flask.*
11. Take 4-5 burette readings and select three concordant readings.
12. Do not bring liquid level in the burette at zero mark for every reading to save your time.
13. It is necessary to take the reading with eye as nearly as possible on a level with the liquid to avoid the error due to parallax as shown in the figure 4.4.
14. Use your index finger to fill the pipette.
15. Wash the apparatus after experiment and record your observations in the note book.

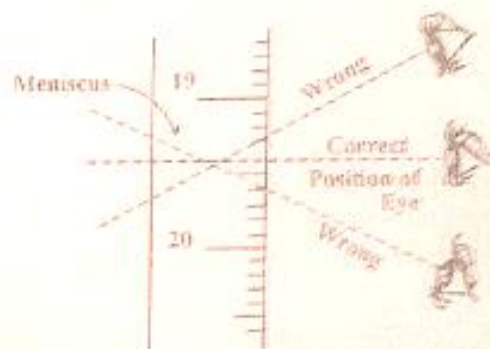


Figure 4.4: How to take measurement from the burette

### 3.3 Advantages of the volumetric analysis

1. The volumetric analysis is rapid and time saving.
2. No laborious work of precipitation, filtration and drying of precipitates is required.
3. Precision and accuracy are good.
4. Handling and operation is very simple.

### 3.4 Applications of volumetric analysis

The volumetric analysis is used to determine:

1. The concentration (i.e. weight of solute in given volume of the solution) of the solution.
2. Percentage purity or impurity of the substances.
3. Solubility of solute at room temperature.
4. Molecular weights and acidity/basicity of the solutions.
5. Composition of two component mixture.
6. Percentage oxidation of the sample.
7. Free alkali in the soap and acetic acid in vinegar.

### Formulae used in volumetric Analysis:

#### 1. Molarity equation

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

Where  $M_1, V_1$  and  $n_1$  are molarity, volume and number of moles of one solution and  $M_2, V_2$  and  $n_2$  are molarity, volume and No of moles of the other solution respectively.

2. Amount of solute per  $\text{dm}^3$  (strength of solution) = Molarity  $\times$  molecular weight



3.  $M_1 V_1 = M_2 V_2$  (for dilution of solution only)  
Where  $M_1$  and  $V_1$  are molarity and volume of the given solution.  $M_2$  and  $V_2$  are molarity and volume of the required solution.

Percentage of a component =  $\frac{\text{Calculated amount per dm}^3}{\text{Given amount per dm}^3} \times 100$

No of water molecules: Weight of hydrated compound per  $\text{dm}^3 = \text{Molarity} \times (\text{Molecular wt.} + 18x)$

## Redox Titrations (Oxidation Reduction Titrations)

### Introduction

Oxidation is defined as the loss of electron/s by the species or increase in the oxidation state of the species where as the gain of electron/s by the species or decrease in the oxidation state of the species is called reduction. A substance which has tendency to lose electron/s is called reducing agent (e.g.,  $\text{FeSO}_4$ ) and a substance which has tendency to gain electron/s is called oxidizing agent (e.g.  $\text{KMnO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ ). For instance  $\text{Fe}^{2+}$  loses an electron and oxidized to  $\text{Fe}^{3+}$ .  $\text{Mn}^{(7+)}\text{O}_4^{-1}$  gains five electrons and reduced itself to  $\text{Mn}^{2+}$

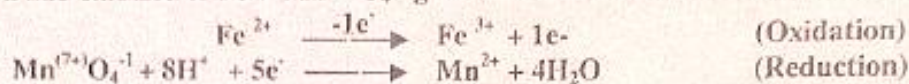


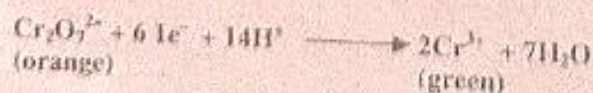
Table: Common Oxidizing and Reducing Reagents

Oxidizing Agents	Molar mass	Reducing Agents	Molar mass
Potassium permanganate, $\text{KMnO}_4$	158.03 g/mol	Sodium thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$	158.10 g/mol
Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$	294.18 g/mol	Ferrous sulphate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278 g/mol
Ceric sulphate, $\text{CeSO}_4$	294.18 g/mol	Mohr's salt, $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$	392 g/mol
Iodine, $\text{I}_2$	253.80 g/mol	Succinic acid, $(\text{CH}_2\text{COOH})_2$	118 g/mol
Potassium iodate, $\text{KIO}_3$	214.00 g/mol	Ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	142 g/mol
Potassium bromate, $\text{KBrO}_3$	167.00 g/mol	Sodium oxalate, $\text{C}_2\text{O}_4\text{Na}_2$	134 g/mol
		Oxalic acid, $\text{C}_2\text{O}_4\text{H}_2 \cdot 2\text{H}_2\text{O}$	126 g/mol

### Potassium dichromate Titrations

Potassium dichromate is weaker oxidizing agent than potassium permanganate but it has several advantages over the latter, i.e. it can be obtained in pure state and remains stable up to its fusion point, and is therefore an excellent primary standard (standard solutions of exactly known strength can be prepared by weighing out the pure and dry salt and dissolving it in water and diluting the solution up to the calculated volume). Furthermore, aqueous solution is stable indefinitely if adequately protected from evaporation. Potassium dichromate is used in acidic solution and is reduced rapidly at the ordinary temperature to a green chromic salt.

It is possible to use dichromate for titrations in presence of hydrochloric without risk of oxidation of  $\text{Cl}^-$  ions. This means that permanganate ( $\text{MnO}_4^-/\text{Mn}^{2+}$  system) is better oxidizing agent than dichromate ( $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  system) since standard electrode potential of ( $\text{MnO}_4^-/\text{Mn}^{2+}$ ) is higher than both  $\text{Cl}_2/2\text{Cl}^-$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$ . Permanganate can oxidize both ferrous and chloride ions. But since standard electrode potential of ( $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$  system) is lower than that of  $\text{Cl}_2/2\text{Cl}^-$  but higher than that of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  systems, dichromate can oxidize ferrous ion but fails to oxidize  $\text{Cl}^-$  ions. So it can be used to oxidize ferrous ion in hydrochloric acid solution. Potassium dichromate is used in acidic medium (in the presence of dil.  $\text{H}_2\text{SO}_4$ ). The reaction may be represented as:





**Indicators:** There is one disadvantage of Potassium dichromate that it does not act as its own indicator owing to the formation of green chromic salt which mask any definite colour change at the end point of the titration. Two types of indicators are used.

- External indicator:**  $K_3[Fe(CN)_6]$  is used as external indicator. Its drops are placed separately on a white tile and sample of titrated solution are withdrawn from time to time with the help of a glass rod and mixed with  $K_3[Fe(CN)_6]$ . At the end point, blue colour is no more produced with  $K_3[Fe(CN)_6]$ .
- Internal indicators:** (i) diphenylamine, (ii) sodium or barium salt of diphenylamine sulphonate acid (iii) diphenylbenzidine etc.

The use of internal indicator gives very satisfactory results, and is now almost universally used in place of the external indicator. One per cent solution of diphenylamine in concentrated sulphuric acid, one per cent solution of diphenylbenzidine in concentrated sulphuric acid or a 0.2 per cent aqueous solution of sodium diphenylamine sulphonate are used as indicators. These indicators are themselves colourless, but, when oxidized by a slight excess of potassium dichromate they produce an intensely coloured purple or blue-violet compounds. It is necessary, however, to prevent ferric ions, which are formed in the course of titration of a ferrous salt, from oxidizing the indicator prematurely, i.e. before dichromate solution is added in excess, and for this purpose phosphoric acid is used. The ferric ions are then converted as fast as they are produced by oxidation into a ferric phosphate complex which is almost undissociated and the ferric ions are thus prevented from oxidizing the indicator. So with these indicators phosphoric acid must be used.

These indicators impart a green colour to the ferrous solution, which deepens to a blue green shortly before the end-point. At the end point an intense purple or blue violet colouration is produced which remains permanent after shaking.

#### Preparation of Standard solutions:

##### 1. 0.1M Solution of Potassium dichromate:

Weigh out 14.71g A.R grade potassium dichromate exactly on a glaze paper and transfer it to a 500 mL volumetric flask. Place a glass funnel over the flask. Place the glaze paper in the glass funnel and wash both sides of it with wash bottle so that washing go to the measuring flask. Raise the funnel and wash the stem of the funnel collecting the washing in the measuring flask. Add about 200 mL distilled water to the flask and shake well to dissolve potassium dichromate completely. When the solid is completely dissolved dilute the solution up to the mark. Close the stopper and shake well. Allow time for the solution to become homogenous

A volumetric flask is used to make up a solution of fixed volume very accurately. This volumetric flask measures 500 mL  $\pm$  0.2 mL. To make up a solution, first dissolve the solid material completely, in less water than required to fill the flask to the mark.

##### 2. 0.1M Solution of Sodium thiosulphate:

Weigh out accurately 15.81g sodium thiosulphate,  $Na_2S_2O_3$  and transfer it to 1000 mL volumetric flask and prepare the 0.1M solution as described above.

##### 3. 0.1M Solution of Ferrous sulphate, $FeSO_4 \cdot 7H_2O$

Weigh out accurately 27.8 g ferrous sulphate,  $FeSO_4 \cdot 7H_2O$  and transfer it to 1000 mL volumetric flask and prepare the 0.1M solution as described above.

##### 4. 0.1M Mohr's salt $FeSO_4 \cdot 7H_2O$

Weigh out accurately 39.2 g Mohr's salt,  $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ , and transfer it to 1000 mL volumetric flask and prepare the 0.1M solution as described above.

##### 5. Indicator Solutions:

- 5%  $K_3[Fe(CN)_6]$ : Dissolve 5 g of the reagent in 100 mL of distilled water.
- 1% Diphenylamine: Dissolve 1 g of the reagent in 100 mL of conc.  $H_2SO_4$
- 1% Diphenylbenzidine: Dissolve 1 g of the reagent in 100 mL of conc.  $H_2SO_4$
- 2% Sodium salt of diphenylamine sulphonate acid: Dissolve 2 g of the reagent in 100 mL of distilled water.



## EXPERIMENT

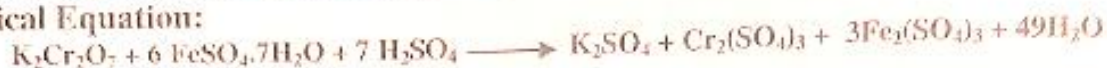


# 1

Determine amount of Fe in the given solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  volumetrically. ✓

**Theory:**  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is titrated with the standard solution of potassium dichromate which oxidizes ferrous sulphate to ferric sulphate. Fe present in the solution is calculated from the volume of the standard potassium dichromate solution used. The end point can be detected by using external indicator (5%  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) or internal indicator (2% Sodium diphenylamine sulphonate).

**Chemical Equation:**



**Mole ratio:**  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:6$

**Standard solution:** 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

**Indicator:**  $\text{K}_3[\text{Fe}(\text{CN})_6]$

**End point:** Drop of reaction mixture does not impart blue colour to indicator.

**Procedure:**

- 10 mL of the given  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution and 10 mL of dil. sulphuric acid was taken in the conical flask
- Standard potassium dichromate solution was run from burette; 2 mL each time.
- A drop of reaction mixture was taken out with the help of glass rod after addition of each 2 mL of potassium dichromate and mixed with a drop of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  taken on white tile which first produce blue colour. Addition of potassium dichromate solution was continued until reaction mixture did not impart blue colour to indicator.
- Titration was repeated three or four times to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Molarity of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution =  $M_1 = 0.01 \text{ M}$   
Volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution =  $V_1 = 10.0 \text{ mL}$   
No. of moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  =  $n_1 = 1$   
Molarity of  $\text{FeSO}_4$  solution =  $M_2 = ?$   
Volume of  $\text{FeSO}_4$  solution taken in the flask =  $V_2 = 10.0 \text{ mL}$   
No. of moles of  $\text{FeSO}_4$  =  $n_2 = 6$

Substituting the values in molarity equation

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$
$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 10} = 0.06 \text{ M}$$

Hence, the molarity of the given solution = 0.06 M

Amount of Fe in the given solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per  $\text{dm}^3$  = Molarity  $\times$  Atomic mass of Fe  
=  $0.06 \times 55.845 \text{ g/mol} = 3.35 \text{ g}$

**Result:** The given solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  contains 3.35 g Fe per  $\text{dm}^3$ .

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.00	10.0	10.0
2	10.0	20.0	10.0
3	20.3	30.3	10.0

Volume used = 10.0 mL

### Alternative Procedure using Internal Indicator (2% Sodium diphenyl sulphonate)

**Indicator:** Sodium diphenyl sulphonate)

**End point:** Violet blue colour

**Procedure:**

- 10 mL of the given  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution, 10 mL of dil. sulphuric acid and about 10 mL phosphoric acid was taken in the conical flask. 2-3 drops of indicator were added to this solution
- Standard potassium dichromate solution was run from burette till the appearance of violet blue colour.

**Note:** Except, indicator, end point and procedure, all other things are similar to experiment 1.



# EXPERIMENT

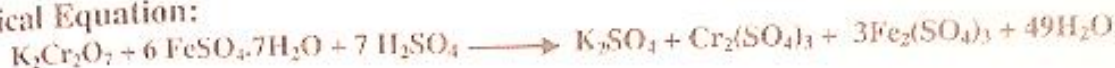


## 2

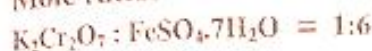
Determine percentage purity of ferrous sulphate 3.5 g of which have been dissolved in 250 mL of the given solution. (Using external indicator)

**Theory:**  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is titrated with the standard solution of potassium dichromate which oxidizes ferrous sulphate to ferric sulphate. Fe present in the solution is calculated from the volume of the standard potassium dichromate solution used. The end point can be detected by using external indicator (5%  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) or internal indicator (2% Sodium diphenylamine sulphonate).

**Chemical Equation:**



**Mole ratio:**



**Standard solution:**

0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

**Indicator:**  $\text{K}_3[\text{Fe}(\text{CN})_6]$

**End point:** Drop of reaction mixture does not impart blue colour to indicator.

**Procedure:**

- 10 mL of the given  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution and 10 mL of dil. sulphuric acid was taken in the conical flask
- Standard potassium dichromate solution was run from burette; 2 mL each time.
- A drop of reaction mixture was taken out with the help of glass rod after addition of each 2 mL of potassium dichromate and mixed with a drop of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  taken on white tile which first produce blue colour. Addition of potassium dichromate solution continued until reaction mixture did not impart blue colour to indicator.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution =  $M_1 = 0.01 \text{ M}$

Volume of potassium dichromate solution =  $V_1 = 10.0 \text{ mL}$

No. of moles of potassium dichromate =  $n_1 = 1$

Molarity of  $\text{FeSO}_4$  solution =  $M_2 = ?$

Volume of  $\text{FeSO}_4$  solution taken in the flask =  $V_2 = 10.0 \text{ mL}$

No. of moles of  $\text{FeSO}_4$  =  $n_2 = 6$

Substituting the values in molarity equation

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 10} = 0.06 \text{ M}$$

Hence, the molarity of the given solution = 0.06 M

Amount of Fe in the given solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per  $\text{dm}^3$  = Molarity  $\times$  Molar mass of ferrous sulphate

$$= 0.06 \times 278 \text{ g/mol} = 16.68 \text{ g}$$

Amount of ferrous sulphate dissolved in 250 mL = 5 g

Amount of ferrous sulphate dissolved in 1000 mL =  $5/250 \times 1000 = 20.0 \text{ g}$

$$\text{Percentage purity} = \frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{16.68}{20.0} \times 100 = 83.4\%$$

**Result:** Percentage purity of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  is 83.4 %

**Alternative Procedure using Internal Indicator (2% Sodium diphenyl sulphonate)**



Indicator: Sodium diphenyl sulphonate)

End point: Violet blue colour

Procedure:

1. 10 mL of the given  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution, 10 mL of dil. sulphuric acid and about 10 mL phosphoric acid was taken in the conical flask. 2-3 drops of indicator were added to this solution
2. Standard potassium dichromate solution was run from burette till the appearance of violet blue colour.
3. Titration was repeated three or four times to get the concordant readings.

Note: Except, indicator, end point and procedure, all other things are similar to experiment 2.

**Exercise:** Determine percentage of ferric and ferrous ions in the given sample of ferrous sulphate 3.5 g of which have been dissolved in 250 mL of the given solution.

Hint: Amount of ferrous ion per  $\text{dm}^3$  = Molarity  $\times$  Atomic mass of  $\text{Fe}^{2+}$

$$\text{Percentage of } \text{Fe}^{2+} = \frac{\text{Calculate amount of } \text{Fe}^{2+} \text{ per } \text{dm}^3}{\text{Given amount of ferrous sulphate per } \text{dm}^3} \times 100 = x\%$$

$$\text{Percentage of } \text{Fe}^{3+} = 100 - \text{Percentage of } \text{Fe}^{2+} = 100 - x$$

## EXPERIMENT

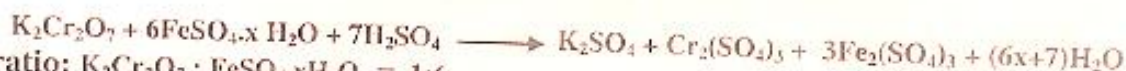


# 3

Determine the value of  $x$  in  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ . 27.8 g of which have been dissolved per  $\text{dm}^3$  of the given solution. (Using internal indicator)

**Theory:**  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  is titrated with the standard solution of potassium dichromate which oxidizes ferrous sulphate to ferric sulphate. The value of  $x$  is calculated from the volume of the standard potassium dichromate solution used. The end point can be detected by using external indicator (5%  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) or internal indicator (2% Sodium diphenylamine sulphonate).

**Chemical Equation:**



Mole ratio:  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{FeSO}_4 \cdot x\text{H}_2\text{O} = 1:6$

Standard solution: 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

Indicator: Sodium diphenylamine sulphonate

End point: Violet blue colour.

Procedure:

1. 10 mL of the given  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  solution, 10 mL of dil. sulphuric acid and 10 mL of phosphoric acid were taken in the conical flask. 2-3 drops of indicator solution were added.
2. Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
3. Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution =  $M_1 = 0.01 \text{ M}$   
 Volume of potassium dichromate solution =  $V_1 = 16.7 \text{ mL}$   
 No. of moles of potassium dichromate =  $n_1 = 1$   
 Molarity of  $\text{FeSO}_4$  solution =  $M_2 = ?$   
 Volume of  $\text{FeSO}_4$  solution taken in the flask =  $V_2 = 10.0 \text{ mL}$   
 No. of moles of  $\text{FeSO}_4$  =  $n_2 = 6$   
 Substituting the values in molarity equation

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	16.7	16.7
2	16.7	33.4	16.7
3	20.0	36.6	16.6

Volume used = 16.7 mL



$$\begin{aligned}
 (K_2Cr_2O_7) \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} (FeSO_4) \\
 M_2 &= \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 16.7 \times 6}{1 \times 10} = 0.10M \\
 &= 0.10M \\
 &= \text{Molarity} \times \text{Molar mass of } FeSO_4 \cdot xH_2O \\
 27.8 \text{ g per dm}^3 &= 0.10 \times (152 + 18x) \\
 27.8/0.10 &= (152 + 18x) \\
 18x &= 278 - 152 = 126 \\
 x &= 126/18 = 7
 \end{aligned}$$

Hence, the molarity of the given solution  
Amount of  $FeSO_4 \cdot xH_2O$  per  $dm^3$

Result: Hence the value of  $x$  in  $FeSO_4 \cdot xH_2O$  is 7

### Alternative Procedure using Internal Indicator ( $K_3[Fe(CN)_6]$ ) solution

Indicator:  $K_3[Fe(CN)_6]$

End point: Drop of reaction mixture does not impart blue colour to indicator.

Procedure:

1. 10 mL of the given  $FeSO_4 \cdot 7H_2O$  solution and 10 mL of dil. sulphuric acid was taken in the conical flask.
2. Standard potassium dichromate solution was run from burette; 2 mL.
3. A drop of reaction mixture was taken out with the help of glass rod after addition of each 2 mL of potassium dichromate and mixed with a drop of  $K_3[Fe(CN)_6]$  taken on white tile which first produce blue colour.
4. Addition of potassium dichromate solution continued until reaction mixture did not impart blue colour to indicator.
5. Titration was repeated three or four times to get the concordant readings.

## EXPERIMENT



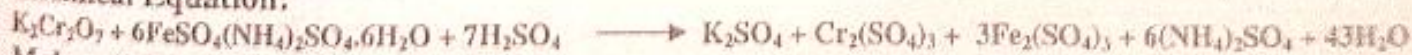
# 4

5.0 g Mohr's salt is dissolved per  $dm^3$  in the given solution. Determine the percentage of Fe in the given sample of Mohr's salt by using 0.01 M solution of potassium dichromate (Using internal indicator).

Theory:

Mohr's salt is a double salt with formula  $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ . The solution of Mohr's salt is titrated with the standard solution of potassium dichromate which oxidizes ferrous sulphate to ferric sulphate. Percentage of Fe present in the solution is calculated from the volume of the standard potassium dichromate solution used. The end point can be detected by using external indicator (5%  $K_3[Fe(CN)_6]$ ) or internal indicator (2 % Sodium diphenylamine sulphonate).

Chemical Equation:



Mole ratio:  $K_2Cr_2O_7 : FeSO_4 \cdot 7H_2O = 1:6$

Standard solution: 0.01M  $K_2Cr_2O_7$  solution.

Indicator: Sodium diphenylamine sulphonate

End point: Violet blue colour.

Procedure:

1. 10 mL of the given Mohr's salt solution, 10 mL of dil. sulphuric acid and 10 mL of phosphoric acid were taken in the conical flask.
2. 2-3 drops of indicator solution were added.
3. Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
4. Titration was repeated three or four times to get the concordant readings.



## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution  $= M_1 = 0.01 \text{ M}$   
 Volume of potassium dichromate solution used  $= V_1 = 10.0 \text{ mL}$   
 No. of moles of potassium dichromate  $= n_1 = 1$   
 Molarity of Mohr's salt solution  $= M_2 = ?$   
 Volume of Mohr's salt solution in the flask  $= V_2 = 10.0 \text{ mL}$   
 No. of moles of Mohr's salt  $= n_2 = 6$   
 Substituting the values in molarity equation

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

$$\begin{aligned}
 \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} \\
 M_2 &= \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 10} = 0.06 \text{ M} \\
 &= 0.06 \text{ M}
 \end{aligned}$$

Hence, the molarity of the given solution  
 Amount of Fe in Mohr's salt per  $\text{dm}^3$

$= \text{Molarity} \times \text{Molar mass of Fe}$   
 $= 0.06 \times 55.84 = 3.35 \text{ g}$

Amount of Mohr's salt per  $\text{dm}^3$  in the given sample  
 5.0 g Mohr's salt contains Fe  
 100 g Mohr's salt contains Fe

$= 5 \text{ g per dm}^3$   
 $= 3.35 \text{ g}$   
 $= 3.35/5 \times 100 = 67 \text{ g}$

Result: Hence the given sample contains 67% Fe

## Alternative Procedure using external indicator

This experiment can be performed by using external indicator. In this procedure will be as given below. Theory, chemical equation and calculations will be same as in experiment 4.

Indicator:  $\text{K}_3[\text{Fe}(\text{CN})_6]$

End point: Drop of reaction mixture does not impart blue colour to indicator.

Procedure:

1. 10 mL of the given Mohr's salt solution and 10 mL of dil. sulphuric acid was taken in the conical flask
2. Standard potassium dichromate solution was run from burette; 2 mL.
3. A drop of reaction mixture was taken out with the help of glass rod after addition of each 2 mL of potassium dichromate and mixed with a drop of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  taken on white tile which first produce blue colour.
4. Addition of potassium dichromate solution continued until reaction mixture did not impart blue colour to indicator.
5. Titration was repeated three or four times to get the concordant readings.

## EXPERIMENT



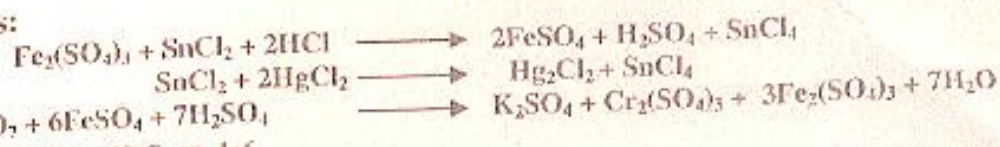
5

2.5 g ammonium iron(III)sulphate has been dissolved in 300 mL of the given solution. Determine the percentage and quantity of Fe in the sample. 2.942 g potassium dichromate per  $\text{dm}^3$  is provided.)

Theory: Ammonium iron(III)sulphate cannot be titrated directly with potassium dichromate directly because iron is present in Ferric state. Ferric ion present in the sample is first reduced to ferrous by  $\text{SnCl}_2$  in presence of conc.  $\text{HCl}$  and excess of  $\text{SnCl}_2$  is destroyed by  $\text{HgCl}_2$ . The ferrous ions are then titrated against standard potassium dichromate solution.



## Chemical Reactions:



Mole ratio:  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:6$

Standard solution: 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

Indicator: Sodium diphenylamine sulphonate

End point: Violet blue colour.

## Procedure:

- 20.0 mL of the given solution and 3 mL of conc. HCl was taken in the conical flask and boiled
- 0.1M  $\text{SnCl}_2$  was run from the burette dropwise to boiling solution until yellow colour of Ferric iron was discharged.
- The solution was cooled under tap water and diluted to 150 mL. 10-20 mL of saturated solution of  $\text{HgCl}_2$  was added until formation of slight white ppt.
- 80 mL dil. sulphuric acid and 5 mL of phosphoric acid were added to reaction mixture in the conical flask.
- 2-3 drops of indicator solution were added.
- Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Mass of potassium dichromate dissolved per  $\text{dm}^3 = 2.942 \text{ g}$

Molarity of potassium dichromate solution  

$$= \frac{2.942}{294.2} = M_1 = 0.01 \text{ M}$$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

Volume of potassium dichromate solution =  $V_1 = 10.0 \text{ mL}$

No. of moles of potassium dichromate =  $n_1 = 1$

Molarity of Ammonium iron(III)sulphate solution =  $M_2 = ?$

Volume of the sample solution taken in the flask =  $V_2 = 20.0 \text{ mL}$

No. of moles of Ammonium iron(III)sulphate =  $n_2 = 6$

Substituting the values in molarity equation

$$\begin{aligned} \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} \\ M_2 &= \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 20} = 0.03 \text{ M} \end{aligned}$$

Hence, the molarity of the given solution

Amount of Fe in sample per  $\text{dm}^3 = \text{Molarity} \times \text{Molar mass of Fe} = 0.03 \times 55.84 = 1.67 \text{ g}$

Amount of Fe in 300 mL of the sample =  $1.67/1000 \times 300 = 0.50 \text{ g}$

Amount of Ammonium iron(III)sulphate in 300 mL = 2.5 g

Amount of Ammonium iron(III)sulphate in 1000 mL =  $2.5/300 \times 1000 = 8.33 \text{ g}$

8.33 g sample contains iron = 1.67 g

100 g sample contains iron (percentage of iron) =  $1.67/8.33 \times 100 = 20 \%$

Result: Hence the given sample contains 20 % Fe and 0.50 g Fe in 300 mL of the sample.

NB: This experiment can be performed by using external indicator. In this case procedure will be as given below. Theory, chemical equation and calculations will be same as in experiment 5.

Indicator:  $\text{K}_3\text{Fe}(\text{CN})_6$

End point: Drop of reaction mixture does not impart blue colour to indicator.



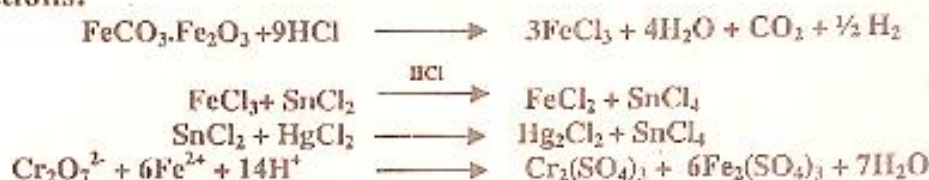
**Procedure:**

1. 20 mL of the reduced sample solution and 10 mL of dil. sulphuric acid was taken in the conical flask
2. Standard potassium dichromate solution was run from burette; 2 mL.
3. A drop of reaction mixture was taken out with the help of glass rod after addition of each 2 mL of potassium dichromate and mixed with a drop of  $K_3[Fe(CN)_6]$  taken on white tile which first produce blue colour.
4. Addition of potassium dichromate solution continued until reaction mixture did not impart blue colour to indicator.
5. Titration was repeated three or four times to get the concordant readings.

**EXPERIMENT****6**

6 g of spathic ore ( $FeCO_3 \cdot Fe_2O_3$ ) has been dissolved per  $dm^3$  of the given solution. Determine the percentage of Fe in the sample, 0.01M  $K_2Cr_2O_7$  is provided.

**Theory:** Spathic ore ( $FeCO_3 \cdot Fe_2O_3$ ) contains both  $Fe^{3+}$  and  $Fe^{2+}$ .  $Fe^{3+}$  cannot be titrated directly with potassium dichromate. A known quantity of spathic ore ( $FeCO_3 \cdot Fe_2O_3$ ) is dissolved in HCl. Ferric ions are first reduced to ferrous by  $SnCl_2$  and excess of  $SnCl_2$  is destroyed by  $HgCl_2$ . The ferrous ions are then titrated against standard potassium dichromate solution.

**Chemical Reactions:**

Mole ratio:  $K_2Cr_2O_7 : FeSO_4 \cdot 7H_2O = 1:6$

Standard solution: 0.01M  $K_2Cr_2O_7$  solution.

Indicator: Sodium diphenylamine sulphonate

End point: Violet blue colour.

**Procedure:**

1. 20.0mL of the given solution and 3 mL of conc. HCl was taken in the conical flask and boiled.
2. 0.1M  $SnCl_2$  was run from the burette dropwise to boiling solution until yellow colour of Ferric iron was discharged.
3. The solution was cooled under tap water and diluted to 150 mL. 10-20 mL of saturated solution of  $HgCl_2$  was added until formation of slight white ppt.
4. 80 mL dil. sulphuric acid and 5 mL of phosphoric acid were added to reaction mixture in the conical flask. 2-3 drops of indicator solution were added.
5. Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
6. Titration was repeated three or four times to get the concordant readings.
- 7.

**OBSERVATIONS AND CALCULATIONS**

Molarity of potassium dichromate solution =  $M_1 = 0.01 \text{ M}$   
 Volume of potassium dichromate solution used =  $V_1 = 10.0 \text{ mL}$   
 No. of moles of potassium dichromate =  $n_1 = 1$   
 Molarity of sample ore solution =  $M_2 = ?$   
 Volume of the solution taken in the flask =  $V_2 = 20.0 \text{ mL}$   
 No. of moles of iron =  $n_2 = 6$   
 Substituting the values in molarity equation

No	Initial reading	Final reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL



$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 20} = 0.03M$$

$$= 0.03M$$

$$= \text{Molarity} \times \text{Molar mass of Fe} = 0.03 \times 55.84 = 1.67 \text{ g}$$

$$= 1.67 \text{ g}$$

$$= 1.67 / 6 \times 100 = 27.5 \%$$

Hence, the molarity of the given solution

Amount of Fe in sample per dm<sup>3</sup>

Amount of Fe in 6 g of the sample

Amount of Fe in 100 g of the sample

Result: Hence the given sample contains 27.5 % Fe.

## EXPERIMENT



# 7

6 g of ferric alum has been dissolved per dm<sup>3</sup> of the given solution. Determine the percentage of Fe in the sample. 0.01M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is provided.

Theory: Ferric alum contains ferric sulphate which cannot be titrated directly with potassium dichromate directly because iron is present in Ferric state. Ferric ions present in the sample are first reduced to ferrous by SnCl<sub>2</sub> in presence of conc. HCl and excess of SnCl<sub>2</sub> is destroyed by HgCl<sub>2</sub>. The ferrous ions are then titrated against standard potassium dichromate solution.

Chemical Reactions:



Mole ratio: K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> : FeSO<sub>4</sub>·7H<sub>2</sub>O = 1:6

Standard solution: 0.01M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution.

Indicator: Sodium diphenylamine sulphonate

End point: Violet blue colour.

Procedure:

- 20.0 mL of the given solution and 3 mL of conc. HCl was taken in the conical flask and boiled
- 0.1M SnCl<sub>2</sub> was run from the burette dropwise to boiling solution until yellow colour of Ferric iron was discharged.
- The solution was cooled under tap water and diluted to 150 mL. 10-20 mL of saturated solution of HgCl<sub>2</sub> was added until formation of slight white ppt.
- 80 mL dil. sulphuric acid and 5 mL of phosphoric acid were added to reaction mixture in the conical flask.
- 2-3 drops of indicator solution were added.
- Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution = M<sub>1</sub> = 0.01

Volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution = V<sub>1</sub> = 10.0 mL

No. of moles of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> = n<sub>1</sub> = 1

Molarity of Ferric alum solution = M<sub>2</sub> = ?

Volume of the sample solution = V<sub>2</sub> = 20.0 mL

No. of moles of Ammonium iron(III)sulphate = n<sub>2</sub> = 6

Substituting the values in molarity equation

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL



(Potassium dichromate)  $\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$  (Ammonium iron(III)sulphate)

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 20} = 0.03M$$

Hence, the molarity of the given solution

Amount of Fe in sample per  $\text{dm}^3$

$$= 0.03M$$

$$= \text{Molarity} \times \text{Molar mass of Fe}$$

$$= 0.03 \times 55.84 = 1.67 \text{ g}$$

Amount of Ferric alum dissolved per  $\text{dm}^3$  in the sample

$$= 6 \text{ g}$$

6 g sample of Ferric alum contains Fe

$$= 1.67 \text{ g}$$

100 g sample contains iron (percentage of iron)

$$= 1.67 / 6 \times 100 = 27.83\%$$

**Result:** Hence the given sample contains 27.83%.

## EXPERIMENT



# 8

The given solution M contains 5.0 g per 250 mL partially oxidized ferrous sulphate. Determine the percentage of oxidation by using 0.01 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution (Using internal indicator).

**Theory:** Only unoxidized  $\text{FeSO}_4$  is titrated with the standard solution of potassium dichromate which oxidizes ferrous sulphate to ferric sulphate. The end point can be detected by using external indicator (5%  $\text{K}_4[\text{Fe}(\text{CN})_6]$ ) or internal indicator (2 % Sodium salt of diphenylamine sulphonate).

**Chemical Equation:**



**Mole ratio:**  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:6$

**Standard solution:** 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

**Indicator:** Sodium diphenylamine sulphonate

**End point:** Violet blue colour.

**Procedure:**

1. 10 mL of the given solution, 10 mL of dil. sulphuric acid and 10 mL of phosphoric acid were taken in the conical flask. 2-3 drops of indicator solution were added to the solution in the flask.
2. Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
3. Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution =  $M_1 = 0.01 \text{ M}$

Volume of potassium dichromate solution =  $V_1 = 10.0 \text{ mL}$

No. of moles of potassium dichromate =  $n_1 = 1$

Molarity of Mohr's salt solution =  $M_2 = ?$

Volume of Ferrous sulphate solution =  $V_2 = 10.0 \text{ mL}$

No. of moles of Mohr's salt =  $n_2 = 6$

Substituting the values in molarity equation

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 10} = 0.06M$$

Hence, the molarity of the given solution

Amount of  $\text{FeSO}_4$  in the sample per  $\text{dm}^3$

$$= 0.06M$$

$$= \text{Molarity} \times \text{Molar mass of Fe} = 0.06 \times 152 = 9.12 \text{ g}$$

No	Initial reading	Final reading	Volume ( mL )
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL



Amount of partially oxidized  $\text{FeSO}_4$  in 250 mL  
 Amount of partially oxidized  $\text{FeSO}_4$  in 1 dm<sup>3</sup>  
 Amount of oxidized  $\text{FeSO}_4$  in 1 dm<sup>3</sup>

$$= 5 \text{ g per dm}^3$$

$$= 5/250 \times 1000 = 20.0 \text{ g}$$

$$= 20.00 - 9.12 = 10.88 \text{ g}$$

Percentage oxidation =  $\frac{\text{Oxidized ferrous sulphate}}{\text{Total ferrous sulphate}} \times 100 = \frac{10.88}{20} \times 100 = 45.6\%$

Result: Hence the given sample of ferrous sulphate is 45.6 % oxidized.

## EXPERIMENT



# 9

2.5 g potassium dichromate has been dissolved in 250 mL of the solution 'S'. Determine percentage purity of potassium dichromate. 0.06 M ferrous sulphate solution is provided. ✓

**Theory:** Standard solution of ferrous sulphate is titrated with the given solution of potassium dichromate which oxidizes ferrous sulphate to ferric sulphate. The end point can be detected by using external indicator (2%  $\text{K}_3\text{Fe}(\text{CN})_6$ ) or internal indicator (2% Sodium diphenylamine sulphonate).

**Chemical Equation:**



Mole ratio:  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:6$

Standard solution: 0.06M ferrous sulphate solution.

Indicator: Sodium diphenylamine sulphonate.

End point: violet blue

**Procedure:**

- 10 mL of the standard  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution, 10 mL of dil. sulphuric acid and about 10 mL phosphoric acid was taken in the conical flask and 2-3 drops of indicator were added to this solution
- Potassium dichromate solution was run from burette till the appearance of violet blue colour.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution =  $M_1 = ?$   
 Volume of potassium dichromate solution used =  $V_1 = 10.0 \text{ mL}$   
 No. of moles of potassium dichromate =  $n_1 = 1$   
 Molarity of  $\text{FeSO}_4$  solution =  $M_2 = 0.06 \text{ M}$   
 Volume of  $\text{FeSO}_4$  solution taken in the flask =  $V_2 = 10.0 \text{ mL}$   
 No. of moles of  $\text{FeSO}_4$  =  $n_2 = 6$   
 Substituting the values in molarity equation

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.06 \times 10 \times 1}{6 \times 10} = 0.01 \text{ M}$$

Hence, the molarity of the given solution

Amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  per dm<sup>3</sup> in the given solution = Molarity  $\times$  Molar mass of ferrous sulphate  
 $= 0.01 \times 294 \text{ g/mol} = 2.94 \text{ g}$

Amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  dissolved in 250 mL

Amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  dissolved in 1000 mL

$$\text{Percentage purity} = \frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{2.94}{10} \times 100 = 29.4\%$$

Result: Percentage purity of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 29.4 %

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.00	10.3	10.3
2	10.3	20.3	10.0
3	20.3	30.3	10.0

Volume used = 10.0 mL



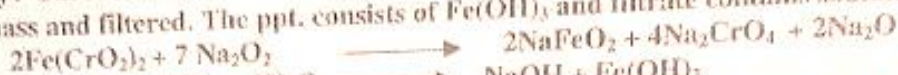
# EXPERIMENT



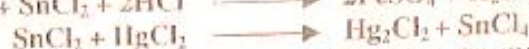
# 10

Determine the amount of iron and chromium in the give sample of chromite ore. You are provided with 0.01 M solution of potassium dichromate.

**Theory:** Chromite ore has the composition of  $\text{Fe}(\text{CrO}_2)_2$ . It is fused with excess of  $\text{Na}_2\text{O}_2$  and water is added to fused mass and filtered. The ppt. consists of  $\text{Fe}(\text{OH})_3$  and filtrate contains sodium chromate.

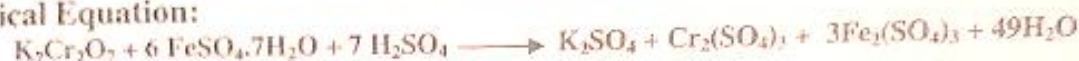


$\text{Fe}(\text{OH})_3$  is dissolved in  $\text{HCl}$  and reduced with  $\text{SnCl}_2$  and titrated with standard potassium dichromate solution.



Solution containing sodium chromate is treated with excess of known volume of ferrous ammonium sulphate and titrated against standard solution of potassium dichromate solution.

**Chemical Equation:**



**Mole ratio:**  $\text{K}_2\text{Cr}_2\text{O}_7 : 6\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:6$

**Standard solution:** 0.06M ferrous sulphate solution.

**Indicator:** Sodium diphenylamine sulphonate

**End point:** violet blue

**Procedure:**

1. Accurately weighed 0.5 g finely powdered chromite ore was mixed with 10 g  $\text{Na}_2\text{O}_2$  and heated the mixture in a thick walled nickel crucible to redness for 10 minutes and allowed to cool. 3 g  $\text{Na}_2\text{O}_2$  was added to the melt and heated again for 10 minutes and allowed to cool.
2. 50 mL water was added to fused mass and boiled until yellow mass was dissolved. To destroy excess of  $\text{NaOH}$ , 4 g of ammonium carbonate was added and boiled. The mixture was filtered and ppt. washed.
3. Precipitate was dissolved in 20 mL  $\text{HCl}$ .
4. 0.1M  $\text{SnCl}_2$  was run from the burette dropwise to boiling solution until yellow colour of Ferric iron was discharged.
5. The solution was cooled under tap water and diluted to 150 mL. 10-20 mL of saturated solution of  $\text{HgCl}_2$  was added until formation of slight white ppt.
6. 80 mL dil. sulphuric acid and 5 mL of phosphoric acid were added to reaction mixture in the conical flask and 2-3 drops of indicator solution were added.
7. Potassium dichromate solution was run from burette till the appearance of violet blue colour.
8. Titration was repeated three or four times to get the concordant readings

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution =  $M_1 = 0.01 \text{ M}$

Volume of potassium dichromate solution =  $V_1 = 10.0 \text{ mL}$

No. of moles of potassium dichromate =  $n_1 = 1$

Molarity of  $\text{FeSO}_4$  solution =  $M_2 = ?$

Volume of sample solution taken in the flask =  $V_2 = 20.0 \text{ mL}$

No. of moles of  $\text{FeSO}_4$  =  $n_2 = 6$

Substituting the values in molarity equation

No	Initial reading	Final reading	Volume (mL)
1	0.00	10.3	10.3
2	10.3	20.3	10.0
3	20.3	30.3	10.0

Volume used = 10.0mL



$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10 \times 6}{1 \times 20} = 0.03 \text{ M}$$

Hence, the molarity of the given solution

$$= 0.03 \text{ M}$$

Amount of Fe per  $\text{dm}^3$  in the given solution

$$= \text{Molarity} \times \text{Molar mass of Fe}$$

$$= 0.03 \times 56 \text{ g/mol} = 1.68 \text{ g}$$

Amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  dissolved in 250 mL

$$= 2.5 \text{ g}$$

Amount of  $\text{K}_2\text{Cr}_2\text{O}_7$  dissolved in 1000 mL

$$= 2.5 / 250 \times 1000 = 10.0 \text{ g}$$

$$\text{Percentage purity} = \frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{2.94}{10} \times 29.4 = 29.4 \%$$

**Result:** Percentage purity of  $\text{K}_2\text{Cr}_2\text{O}_7$  is 29.4%.

## EXPERIMENT



# 11

The given solution contains 20 g Mohr's salt per  $\text{dm}^3$ . Determine the percentage of ferrous ion in the Mohr's salt by using  $\text{KMnO}_4$ .

**Theory:** This is redox titration.  $\text{KMnO}_4$  oxidizes ferrous ion into ferric ion.

**Chemical Equation:**



Mole ratio:  $\text{KMnO}_4$  : Mohr's salt = 2 : 10

Indicator:  $\text{KMnO}_4$

End point: Light pink colour

Standard solution: 0.02 M  $\text{KMnO}_4$

### Procedure

- 10.0 mL of Mohr's salt solution was taken in the titration flask with pipette and half test tube of dil.  $\text{H}_2\text{SO}_4$  was added to it.
- This solution was titrated against  $\text{KMnO}_4$  solution taken in the burette till end point, light pink colour, was reached.
- Volume of  $\text{KMnO}_4$  used was found by subtracting initial burette reading from final burette reading.
- Titration was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of Mohr's salt	$= V_1$	$= 10.0 \text{ mL}$
Molarity of Mohr's Salt	$= M_1$	$= ?$
No. of moles of Mohr's Salt	$= n_1$	$= 10$
Volume of $\text{KMnO}_4$ used	$= V_2$	$= 10.0 \text{ mL}$
Molarity of $\text{KMnO}_4$	$= M_2$	$= 0.02 \text{ M}$
No. of moles of $\text{KMnO}_4$	$= n_2$	$= 2$

Substituting these values in molarity equation

$$(\text{Mohr's salt}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KMnO}_4)$$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.00	10.3	10.3
2	10.3	20.3	10.0
3	20.3	30.3	10.0

Volume used = 10.0 mL



$$M_1 = \frac{M_2 V_2}{n_2} \times \frac{n_1}{V_1} = \frac{0.02 \times 10 \times 10}{2 \times 10} = 0.1 \text{ M}$$

Molarity of Mohr's salt solution = 0.1 M

Amount of ferrous ions per  $\text{dm}^3$  = Molarity  $\times$  atomic mass =  $0.1 \text{ M} \times 56 = 5.6 \text{ g per dm}^3$

Percentage of ferrous in the sample =  $\frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{5.6}{20} \times 100 = 18\%$

Result: Given sample of Mohr's salt is contains 18% ferrous ions.

## EXPERIMENT



The given solution contains 10 g of  $\text{K}_2\text{C}_2\text{O}_4$  dissolved per  $\text{dm}^3$ . Determine the percentage purity of the commercial salt.

*using  $\text{KMnO}_4$  solution.*

*potassium oxalate*

Theory: This is redox titration  $\text{KMnO}_4$  oxidizes  $\text{K}_2\text{C}_2\text{O}_4$  into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .  $\text{Na}_2\text{SO}_4$  remains inactive.

Chemical Equation:



Mole ratio:  $\text{KMnO}_4$  :  $\text{Na}_2\text{C}_2\text{O}_4$  = 2 : 5

Indicator:  $\text{KMnO}_4$  it self

End point: Light pink colour

Standard solution: 0.02 M  $\text{KMnO}_4$

Procedure:

- 10.0 mL of the given solution was taken in the titration flask with pipette and half test tube of dil  $\text{H}_2\text{SO}_4$  was added to it. The contents were heated unto  $60 - 70^\circ\text{C}$
- This solution was titrated against  $\text{KMnO}_4$  solution taken in the burette till light pink colour end point was reached.
- Volume of  $\text{KMnO}_4$  used was found by subtracting initial burette reading from final burette reading.
- Titration was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of $\text{K}_2\text{C}_2\text{O}_4$ solution	= $V_1$ = 10.0 mL
Molarity of $\text{K}_2\text{C}_2\text{O}_4$	= $M_1$ = ?
No. of moles of $\text{K}_2\text{C}_2\text{O}_4$	= $n_1$ = 5
Volume of $\text{KMnO}_4$ used	= $V_2$ = 10.0 mL
Molarity of $\text{KMnO}_4$	= $M_2$ = 0.02 M
No. of moles of $\text{KMnO}_4$	= $n_2$ = 2

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.00	10.3	10.3
2	10.3	20.3	10.0
3	20.3	30.3	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{K}_2\text{C}_2\text{O}_4) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KMnO}_4)$$

$$M_1 = \frac{M_2 V_2}{n_2} \times \frac{n_1}{V_1} = \frac{0.02 \times 10 \times 5}{2 \times 10} = 0.05 \text{ M}$$

Hence molarity of potassium oxalate = 0.05 M

Amount of potassium oxalate per  $\text{dm}^3$  = Molarity  $\times$  Molar mass =  $0.05 \text{ M} \times 166.21 \text{ g per mol} = 8.31 \text{ g/dm}^3$

Amount of potassium oxalate dissolved per  $\text{dm}^3$  = 10 g

Percentage purity of  $\text{K}_2\text{C}_2\text{O}_4$  =  $\frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{8.31}{20} \times 100 = 41.55\%$

Result: The given sample contains 41.55% pure  $\text{K}_2\text{C}_2\text{O}_4$ .



# EXPERIMENT



# 13

The given solution contains 20 g ferric alum per  $\text{dm}^3$ . Determine the percentage of ferric ion in the sample by using  $\text{KMnO}_4$ .

**Theory:** Ferric alum contains ferrous and ferric ions. Ferrous ions can be estimated by using  $\text{KMnO}_4$  where as ferric cannot be titrated directly with  $\text{KMnO}_4$ . All iron is converted into  $\text{Fe}^{2+}$  by reduction. (Estimation of iron) before and after reduction gives us the  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and total iron.

Ferric ions present in the sample are first reduced to ferrous by  $\text{SnCl}_2$  in presence of conc.  $\text{HCl}$  and excess of  $\text{SnCl}_2$  is destroyed by  $\text{HgCl}_2$ . Chloride ions introduced into the solution from  $\text{SnCl}_2$ ,  $\text{HCl}$  and  $\text{HgCl}_2$  interfere with  $\text{KMnO}_4$  because a part of  $\text{KMnO}_4$  is used to oxidize chloride into chlorine. Presence of chloride ion is made harmless by using Zimmermann-Reinhardt's reagent. The ferrous ions are then titrated against standard  $\text{KMnO}_4$  solution.

## Zimmermann-Reinhardt's Reagent:

Dissolve 50 g  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  in 250 mL distilled water and add cool mixture of 100 mL conc.  $\text{H}_2\text{SO}_4$  and 300 mL water. Then add 100 mL conc.  $\text{H}_3\text{PO}_4$ .

## Chemical Reactions:



Mole ratio:  $\text{KMnO}_4 : \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 2:5$

Standard solution: 0.01M  $\text{KMnO}_4$  solution.

Indicator:  $\text{KMnO}_4$

End point: Faint pink colour

Procedure:

- 10.0 mL of the given solution and 3 mL of conc.  $\text{HCl}$  was taken in the conical flask and boiled.
- 0.1M  $\text{SnCl}_2$  was run from the burette dropwise to boiling solution until yellow colour of Ferric iron was discharged.
- The solution was cooled under tap water and diluted to 150 mL. 10-20 mL of saturated solution of  $\text{HgCl}_2$  was added until formation of slight white ppt.
- 40 mL of Zimmermann-Reinhardt's Reagent was added to reaction mixture in the conical flask.
- Standard potassium permanganate solution was run from burette until the colour of  $\text{KMnO}_4$  was discharged.
- Titration was repeated three or four times to get the concordant readings.



## OBSERVATIONS AND CALCULATIONS

Molarity of $\text{KMnO}_4$ solution	= $M_1 = 0.02\text{M}$
Volume of $\text{KMnO}_4$ solution used	= $V_1 = 10.0\text{ mL}$
No. of moles of $\text{KMnO}_4$	= $n_1 = 2$
Molarity of Ferric alum solution	= $M_2 = ?\text{ M}$
Volume of the sample solution in the flask	= $V_2 = 10.0\text{ mL}$
No. of moles of iron(II)sulphate	= $n_2 = 5$

Substituting the values in molarity equation

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.02 \times 10 \times 5}{2 \times 10} = 0.05\text{M}$$

Hence, the molarity of the Fe in the given solution = 0.05M

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

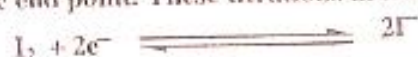


$$\begin{aligned}
 \text{Amount of Fe in sample per dm}^3 &= \text{Molarity} \times \text{Molar mass of Fe} = 0.05 \times 55.84 = 2.792 \text{ g} \\
 \text{Amount of Ferric alum dissolved per dm}^3 \text{ in the sample} &= 10 \text{ g} \\
 \text{Percentage of Fe in the ferric alum} &= \frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{2.792}{10} \times 100 = 27.92\%
 \end{aligned}$$

**Result:** Hence the given sample contains 27.92% Fe.

## IODINE TITRATIONS

Iodine titration is a method of volumetric chemical analysis where the appearance or disappearance of elementary iodine indicates the end point. These titrations are based on redox reaction involving iodine.



The direct iodometric titration method (sometimes termed *iodimetry*) refers to titrations with a standard solution of iodine.

The indirect iodometric titration method (sometimes termed *iodometry*) deals with the titration of iodine liberated in chemical reactions. The normal iodine in aqueous solution acts as a mild oxidising agent and it is reduced quantitatively by reducing agents like  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}$  and  $\text{SnCl}_2$ . There are two types of iodine titrations.

(i) **Iodimetry:** Titrations in which standard solution of iodine is titrated against reducing agents ( $\text{Na}_2\text{S}_2\text{O}_3$ ) are called iodimetry or iodimetric titrations, e.g.  $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \longrightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI}$

Standard iodine solution is taken in the titration flask. Strong reducing agents, e.g.,  $\text{Na}_2\text{S}_2\text{O}_3$  react with iodine solution in acidic medium but weak reducing agents react in weakly acidic or neutral medium.

(ii) **Iodometry:** Estimation of oxidising agents, e.g.,  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{O}_2$ ,  $\text{CuSO}_4$  etc. by titrating iodine, liberated by addition of KI to aq. solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$  or  $\text{CuSO}_4$ , against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$ , is called iodometry. In these titrations 5% KI solution is added to aq. solution of  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{CuSO}_4$ .

which liberates equivalent amount of iodine in acidic medium. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette.

**Chemical Reactions:**



**Indicator & end point:** 1% aqueous starch solution is used as indicator in all types of iodine titrations. It produces intense blue colour with iodine (due to formation of blue complex with iodine molecules - though polyvinyl alcohol). Always use freshly prepared starch solution because starch solution is decomposed by bacterial action if kept for long time.

When iodine solution is taken in the burette, one mL of starch solution is added to flask before titration. End point is appearance of blue colour. But when iodine is liberated in flask or iodine solution is taken in the titration flask, indicator is added near the end point (when colour of solution in the flask becomes lemon yellow). In this case end point is just colourless (Very light blue colour).

### Preparation of Solutions for Iodine Titrations

(i) **Indicator Solution (Starch):** Mix about 1 gram starch with cold water and put the paste in 100 g of boiling water and continue boiling for 15 minutes. Allow to cool and decant clear milky solution. Prepare fresh starch solution for use.

(ii) **Standard Iodine Solution:** Place 10 g of pure KI in a 500 mL glass stoppered flask and add 20 mL distilled water to the flask and put 6.35 g solid iodine in the flask containing KI solution. Insert the stopper and shake well to dissolve iodine. Make up the volume up to the mark. This is approximately 0.05 M iodine solution. This is standardized with standard  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution.

(iii) **Sodium thiosulphate Solution:** Dissolve 24.8 g pure crystals of sodium thiosulphate in 100 mL distilled water in 1 dm<sup>3</sup> measuring flask and make the volume up to the mark. This is 0.1 M  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution.



# EXPERIMENT

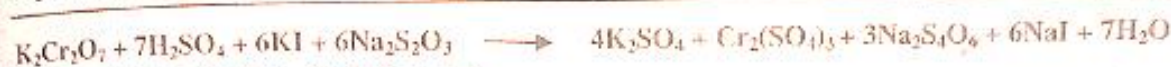


1

20 g hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) per  $\text{dm}^3$  has been dissolved in the given solution. Determine the percentage purity of the sample of sodium thiosulphate. 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is provided.

**Theory:** This is *Iodometric* titration. In these titrations 5% KI solution is added to aq. solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ , which liberates equivalent amount of iodine in acidic medium. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette.

**Chemical Reactions:**



Mole ratio:  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{Na}_2\text{S}_2\text{O}_3 = 1:6$

Standard solution: 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$

Indicator: Starch solution

End point: Light blue colour

**Procedure:**

- 10 mL of the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and 10 mL of dil. sulphuric acid was taken in the iodine flask and about 1-2 g KI was added to the flask.
- $\text{Na}_2\text{S}_2\text{O}_3$  was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution	$= M_1 = 0.01 \text{ M}$
Volume of potassium dichromate solution	$= V_1 = 10.0 \text{ mL}$
No. of moles of potassium dichromate	$= n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution	$= M_2 = ? \text{ M}$
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used	$= V_2 = 10.0 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3$	$= n_2 = 6$

Substituting the values in molarity equation

$$\begin{aligned} \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} \\ M_2 &= \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10.0 \times 6}{1 \times 10} = 0.06 \text{ M} \end{aligned}$$

Hence, the molarity of the given solution  $= 0.06 \text{ M}$   
 Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  per  $\text{dm}^3$   $= \text{Molarity} \times \text{Molar mass of } \text{Na}_2\text{S}_2\text{O}_3$   
 $= 0.06 \times 248 = 14.88 \text{ g per dm}^3$

Dissolve amount of sample of  $\text{Na}_2\text{S}_2\text{O}_3$  per  $\text{dm}^3 = 20.0 \text{ g per dm}^3$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

$$\begin{aligned} \text{Percentage purity of} &= \frac{\text{calculated amount of substance per dm}^3}{\text{Dissolved amount of substance per dm}^3} \times 100 \\ &= \frac{14.88}{20} \times 100 = 74.4\% \end{aligned}$$

Hence percentage purity of  $\text{Na}_2\text{S}_2\text{O}_3$

**Result:** Percentage purity of  $\text{Na}_2\text{S}_2\text{O}_3$  is 74.4%



# EXPERIMENT

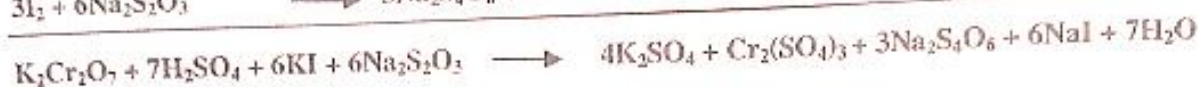
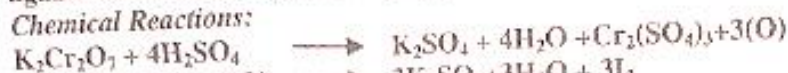


2

30 g  $K_2Cr_2O_7$  per  $dm^3$  has been dissolved in the given solution. Determine the percentage purity of the sample. 0.06 M  $Na_2S_2O_3$  solution is provided

**Theory:** This is *Iodometric* titration. In these titrations 5% KI solution is added to aq. solution of  $K_2Cr_2O_7$  which liberates equivalent amount of iodine in acidic medium. The liberated iodine is immediately titrated against standard solution of  $Na_2S_2O_3$  taken in the burette.

**Chemical Reactions:**



Mole ratio:  $K_2Cr_2O_7 : Na_2S_2O_3 = 1:6$

Standard solution: 0.01M  $K_2Cr_2O_7$

Indicator: Starch solution

End point: Light blue colour

**Procedure:**

- 10 mL of the standard  $K_2Cr_2O_7$  solution and 10 mL of dil. sulphuric acid was taken in the iodine flask and about 1-2 g KI was added to the flask.
- $Na_2S_2O_3$  was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $Na_2S_2O_3$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution =  $M_1 = ?$

Volume of potassium dichromate solution =  $V_1 = 10.0$  mL

No. of moles of potassium dichromate =  $n_1 = 1$

Molarity of  $Na_2S_2O_3$  solution =  $M_2 = 0.06$  M

Volume of  $Na_2S_2O_3$  solution used =  $V_2 = 10.0$  mL

No. of moles of  $Na_2S_2O_3$  =  $n_2 = 6$

Substituting the values in molarity equation

$$(\text{Potassium dichromate}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{Sodium thiosulphate})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.06 \times 10.0 \times 1}{6 \times 10} = 0.01M$$

Hence, the molarity of the given solution = 0.01M

Amount of  $Na_2S_2O_3$  per  $dm^3$  = Molarity  $\times$  Molar mass of  $Na_2S_2O_3$

Dissolve amount of sample of  $K_2Cr_2O_7$  per  $dm^3$  =  $0.01 \times 294 = 29.4$  g per  $dm^3$   
25.0 g per  $dm^3$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

$$\text{Percentage purity} = \frac{\text{Calculated amount of substance per } dm^3}{\text{Dissolved amount of substance per } dm^3} \times 100 = \frac{29.4}{30.0} \times 100 = 98\%$$

**Result:** Percentage purity of  $K_2Cr_2O_7$  is 98%



# EXPERIMENT

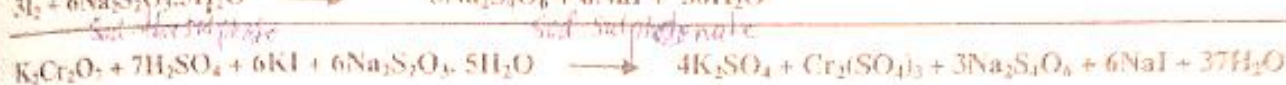
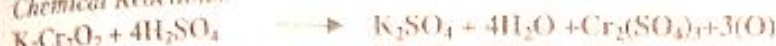


## 3

20 g hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) per  $\text{dm}^3$  has been dissolved in the given solution. Determine the percentage of impurities in the sample of sodium thiosulphate. 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is provided.

**Theory:** This is *Iodometric titration*. In these titrations 5% KI solution is added to aq. solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  which liberates equivalent amount of iodine in acidic medium. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette.

**Chemical Reactions:**



Mole ratio:  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 1:6$

Standard solution: 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$

Indicator: Starch solution

End point: Light blue colour

**Procedure:**

- 10 mL of the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and 10 mL of dil. sulphuric acid was taken in the iodine flask and about 1-2 g KI was added to the flask.
- $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of $\text{K}_2\text{Cr}_2\text{O}_7$ solution	$= M_1 = 0.01 \text{ M}$
Volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution used	$= V_1 = 10.0 \text{ mL}$
No. of moles of $\text{K}_2\text{Cr}_2\text{O}_7$	$= n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution	$= M_2 = ?$
Volume of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution used	$= V_2 = 10.0 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$= n_2 = 6$
Substituting the values in molarity equation	

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

$$(\text{Potassium dichromate}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{Sodium thiosulphate})$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10.0 \times 6}{1 \times 10} = 0.06 \text{ M}$$

Hence, the molarity of the given solution of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 0.06 \text{ M}$

Amount of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  per  $\text{dm}^3 = \text{Molarity} \times \text{Molar mass of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 0.06 \times 248 = 14.88 \text{ g per dm}^3$

Dissolved amount of sample of  $\text{Na}_2\text{S}_2\text{O}_3$  per  $\text{dm}^3 = 20.0 \text{ g per dm}^3$

$$\text{Percentage purity of} = \frac{\text{calculated amount of substance per dm}^3}{\text{Dissolved amount of substance per dm}^3} \times 100 = \frac{14.88}{20.0} \times 100 = 74.4\%$$

$$\text{Percentage of impurities} = 100 - \% \text{purity} = 100 - 74.4 = 25.6\%$$

**Result:** Percentage of impurities in the hypo is 25.6%



# EXPERIMENT



# 4

14.9 g hypo ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) per  $\text{dm}^3$  has been dissolved in the given solution. Determine the value of 'x' in  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  sample. 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution is provided.

**Theory:** This is *Iodometric* titration. In these titrations 5% KI solution is added to aq. solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  which liberates equivalent amount of iodine in acidic medium. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette.

**Chemical Reaction:**



**Mole ratio:**  $\text{K}_2\text{Cr}_2\text{O}_7 : \text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O} = 1:6$

**Standard solution:** 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$

**Indicator:** Starch solution

**End point:** Light blue colour

**Procedure:**

- 10 mL of the standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution and 10 mL of dil. sulphuric acid was taken in the iodine flask and about 1-2 g KI was added to the flask.
- $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of potassium dichromate solution	$= M_1 = 0.01 \text{ M}$
Volume of potassium dichromate solution	$= V_1 = 10.0 \text{ mL}$
No. of moles of potassium dichromate	$= n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution	$= M_2 = ?$
Volume of $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ solution used	$= V_2 = 10.0 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$	$= n_2 = 6$
Substituting the values in molarity equation	

No	Initial reading	Final reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

$$(\text{Potassium dichromate solution}) \quad \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \quad (\text{Sodium thiosulphate})$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10.0 \times 6}{1 \times 10} = 0.06 \text{ M}$$

Hence, the molarity of the given solution of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O} = 0.06 \text{ M}$

Amount of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  per  $\text{dm}^3 = 14.9 \text{ g per dm}^3$

Amount of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  per  $\text{dm}^3 = \text{Molarity} \times \text{Molar mass of } \text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O} = 0.06 \times (158 + 18x) = 14.9$

$$\begin{aligned} \frac{14.9}{0.06} &= \frac{(158 + 18x)}{1} = 248 \\ 248 &= 158 + 18x \\ 248 - 158 &= 18x \\ 90 &= 18x \\ x &= \frac{90}{18} = 5 \end{aligned}$$

**Result:**

The value of x on  $\text{Na}_2\text{S}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  is 5



The given solution contains 10 g mixture of  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_4$  dissolved in 250 mL. Determine the percentage composition of the given mixture. 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  standard solution is provided.

**Theory:** This is *Iodometric* titration. In these titrations 5% KI solution is added to aq. solution of  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_4$  which liberates equivalent amount of iodine. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette.  $\text{Na}_2\text{SO}_4$  remains inactive as impurity.

**Chemical Reactions:**



Mole ratio:  $\text{CuSO}_4 : \text{Na}_2\text{S}_2\text{O}_3 = 1:1$

Standard solution: 0.05  $\text{Na}_2\text{S}_2\text{O}_3$  M

Indicator: Starch solution

End point: Light blue colour

**Procedure:**

- 10 mL of the given mixture solution was taken in the iodine flask and about 1-2 g KI was added.
- Standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution was run from burette until the solution acquired lemon yellow colour.
- 1-2 mL starch solution was added at this point which imparted blue colour to the solution.
- $\text{Na}_2\text{S}_2\text{O}_3$  solution was added further from burette until blue colour just disappeared.
- Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Molarity of $\text{CuSO}_4$ solution	$= M_1 = ?$
Volume of $\text{CuSO}_4$ solution used	$= V_1 = 10.0 \text{ mL}$
No. of moles of $\text{CuSO}_4$	$= n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution	$= M_2 = 0.05 \text{ M}$
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used	$= V_2 = 10.0 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3$	$= n_2 = 1$

No	Initial reading	Final reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

Substituting the values in molarity equation

$$(\text{CuSO}_4) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{Na}_2\text{S}_2\text{O}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 10.0 \times 1}{1 \times 10} = 0.05 \text{ M}$$

Hence, the molarity of the given solution

$$= 0.05 \text{ M}$$

Amount of  $\text{CuSO}_4$  per dm<sup>3</sup> = Molarity  $\times$  Molar mass of  $\text{Na}_2\text{S}_2\text{O}_3 = 0.05 \times 159.6 = 7.98 \text{ g per dm}^3$

Dissolved amount of sample of in 250 mL

$$= 10.0 \text{ g per dm}^3$$

$$\text{Dissolve amount of sample of in } 1000 \text{ cm}^3 = \frac{10}{250} \times 1000 = 40.0 \text{ g}$$

40.0 g sample contains  $\text{CuSO}_4 = 7.98 \text{ g}$

100.0 g sample contains  $\text{CuSO}_4 = 7.98/40 \times 100 = 19.95 \text{ g}$

Hence Percentage of  $\text{CuSO}_4$  in the sample = 19.95%

Therefore percentage of  $\text{Na}_2\text{SO}_4 = 100 - 19.95 = 80.05\%$

**Result:** The given sample contains 19.95%  $\text{CuSO}_4$  and 80.05%  $\text{Na}_2\text{SO}_4$ .



# EXPERIMENT



# 6

Determine solubility of  $\text{CuSO}_4$ . You are provided with 0.05M  $\text{Na}_2\text{S}_2\text{O}_3$  standard solution.

**Theory:** This is *Iodometric* titration. In these titrations 5% KI solution is added to aq. solution of  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_4$  which liberates equivalent amount of iodine. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette,  $\text{Na}_2\text{SO}_4$  remains inactive as impurity.

**Chemical Reactions:**



Mole ratio:  $\text{CuSO}_4 : \text{Na}_2\text{S}_2\text{O}_3 = 1:1$

Standard solution: 0.05  $\text{Na}_2\text{S}_2\text{O}_3$ M

Indicator: Starch solution

End point: Light blue colour

**Procedure:**

- 20 mL distilled water was taken in a beaker and  $\text{CuSO}_4$  was added to the beaker with constant stirring until no more  $\text{CuSO}_4$  was dissolved and some of  $\text{CuSO}_4$  remained undissolved. Solution was filtered, 5 mL of this saturated solution was transferred to a 100 mL measuring flask and volume was made 100 mL by adding water.
- 10 mL of this solution was taken in the iodine flask and about 1-2 g KI was added.
- Standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution was run from burette until the solution acquired lemon yellow colour.
- 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of $\text{CuSO}_4$ solution	$= M_1 = ?$
Volume of $\text{CuSO}_4$ solution used	$= V_1 = 10.0 \text{ mL}$
No. of moles of $\text{CuSO}_4$	$= n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution	$= M_2 = 0.05 \text{ M}$
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used	$= V_2 = 20.0 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3$	$= n_2 = 1$

Substituting the values in molarity equation

$$\begin{aligned} (\text{CuSO}_4) \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} (\text{Na}_2\text{S}_2\text{O}_3) \\ M_1 &= \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 20.0 \times 1}{1 \times 10} = 0.10 \text{ M} \end{aligned}$$

Hence, the molarity of the given solution

Amount of  $\text{CuSO}_4$  per  $\text{dm}^3$

$$= 0.05 \text{ M}$$

$$= \text{Molarity} \times \text{Molar mass of } \text{Na}_2\text{S}_2\text{O}_3$$

$$= 0.10 \times 159.6 = 15.96 \text{ g per dm}^3$$

As the solution was diluted 20 times,

Hence the amount of  $\text{CuSO}_4$  per  $\text{dm}^3$  in saturated solution  $= 20 \times 15.96 \text{ g per dm}^3 = 319.2 \text{ g}$

As the density of water is taken as 1, Amount of  $\text{CuSO}_4$  per 100 g  $= 319.2 / 1000 \times 100 = 31.9 \text{ g}$

**Result:** Hence solubility of  $\text{CuSO}_4$  is 31.9 g per 100 g of water.

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	20.0	20.0
2	20.0	31.1	20.1
3	20.1	31.1	20.0

Volume used = 20.0 mL



# EXPERIMENT



## 7

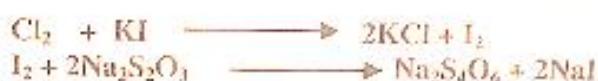
Determine percentage of chlorine in the given sample of bleaching powder. You are provided with 0.05  $\text{Na}_2\text{S}_2\text{O}_3$  M standard solution.

**Theory:** Bleaching powder is a mixture of calcium hypochlorite [ $\text{Ca}(\text{OCl}_2)$ ] and basic calcium chloride [ $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ]. It ionizes in aqueous solution and produce  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{OCl}^-$  and  $\text{Cl}^-$ .  $\text{OCl}^-$  and  $\text{Cl}^-$  produce free chlorine in acidic medium in water. This is called "available chlorine".



Solution containing free chlorine is treated with KI solution in the presence of acetic acid to liberate  $\text{I}_2$  which is titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution.

**Chemical Reactions:**



**Mole ratio:**  $\text{I}_2 : \text{Na}_2\text{S}_2\text{O}_3 = 1:2$

**Standard solution:**  $\text{Na}_2\text{S}_2\text{O}_3$  0.05M

**Indicator:** Starch solution

**End point:** Light blue colour

**Procedure:**

- 3 g bleaching powder was finely crushed and dissolved in 50 mL of water with the help of pestle and mortar and allowed to stand. The aqueous solution was decanted in 250 mL measuring flask. The residue was again ground with water and aqueous solution was transferred to the flask. The procedure was repeated till whole of the bleaching powder was transferred to the measuring flask. Water was added to the measuring flask up to the mark and flask was shaken well.
- 10 mL of this solution was taken in the iodine flask and 10 mL of 10% KI and 3 mL dil.  $\text{H}_2\text{SO}_4$  or  $\text{CH}_3\text{COOH}$  was added.
- Standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Repeat the experiment three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of bleaching powder solution	= $M_1 = ?$
Volume of bleaching powder solution	= $V_1 = 10.0 \text{ mL}$
No. of moles of $\text{I}_2$ (Equivalent to $\text{Cl}_2$ )	= $n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3$ solution	= $M_2 = 0.05 \text{ M}$
Volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution used	= $V_2 = 10.0 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3$	= $n_2 = 2$

Substituting the values in molarity equation

$$(\text{Bleaching powder}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \quad (\text{Sodium thiosulphate})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 10.0 \times 1}{2 \times 10} = 0.025 \text{ M}$$

Hence, the molarity of the given solution with respect to  $\text{Cl}_2 = 0.025 \text{ M}$

$$\text{Amount of } \text{Cl}_2 \text{ per } \text{dm}^3 = \text{Molarity} \times \text{Molar mass of } \text{Cl}_2 = 0.025 \times 71 = 1.775 \text{ g per } \text{dm}^3$$

$$\text{Amount of bleaching powder taken in } 250 \text{ mL} = 2.0 \text{ g}$$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL



$$\text{Amount of bleaching powder taken in } 1000 \text{ cm}^3 = \frac{2}{250} \times 1000 = 8.0 \text{ g}$$

$$\text{Percentage purity of } \text{Cl}_2 = \frac{\text{Calculated amount of } \text{Cl}_2 \text{ per dm}^3}{\text{Dissolved amount of bleaching powder per dm}^3} \times 100 = \frac{1.775}{8} \times 100 = 22.18\%$$

**Result:** Hence the percentage of  $\text{Cl}_2$  in bleaching powder is 22.18%

## EXPERIMENT



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Standardize the given solution of Iodine. 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$  solution is provided.

**Theory:** This is iodimetric redox titration. Iodine solution is titrated against sodium thiosulphate solution taken in the burette.

**Chemical Reactions:**



**Mole ratio:**  $\text{Na}_2\text{S}_2\text{O}_3 : \text{I}_2 = 2 : 1$

**Standard Solution:** 0.1M  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

**Indicator:** Starch solution.

**End Point:** Light Blue colour or just colourless

**Procedure:**

- 10.0 mL iodine solution was taken in the iodine titration flask and 10.0 mL distilled water was added to it.
- Iodine solution was titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution taken in the burette until appearance of lemon yellow colour.
- 1 mL freshly prepared starch solution was added to the flask when lemon yellow colour appeared.
- This solution was again titrated until end point.
- Initial and final burette readings were noted.
- Volume used was found by subtracting initial burette reading from final burette reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of iodine solution	$= M_1 = ?$
Volume of iodine taken in the flask	$= V_1 = 10.0 \text{ mL}$
No. of moles of iodine	$= n_1 = 1$
Molarity of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution	$= M_2 = 0.1\text{M}$
Volume of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution	$= V_2 = 10 \text{ mL}$
No. of moles of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$= n_2 = 2$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

(Iodine solution)  $\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$  (sodium thiosulphate)

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{2 \times 10} = 0.05\text{M}$$

**Result:** Molarity of the given iodine solution is 0.05 M.



## EXPERIMENT

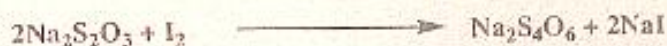


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Given solution contains 25 g impure hypo dissolved per  $\text{dm}^3$ . Find out percentage purity of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ . (0.05M Iodine solution is provided)

**Theory:** This is iodimetric redox titration. Iodine solution is titrated against sodium thiosulphate solution taken in the burette.

**Chemical Reaction:**



**Mole ratio:**  $\text{Na}_2\text{S}_2\text{O}_3$  : Iodine = 2 : 1

**Standard Solution:** 0.05 M Iodine solution.

**Indicator:** Starch solution

**End Point:** Light blue colour or just colour less.

**Procedure:**

- 10.0 mL iodine solution was taken in the iodine titration flask and 10.0 mL distilled water was added to it.
- Iodine solution was titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution taken in the burette until appearance of lemon yellow colour.
- 1 mL freshly prepared starch solution was added to the flask when lemon yellow colour appeared.
- This solution was again titrated until end point.
- Initial and final burette readings were noted.
- Volume used was found by subtracting initial burette reading from final burette reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution =  $M_1 = ?$   
 Volume of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution =  $V_1 = 10.0 \text{ mL}$   
 No. of mole of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  =  $n_1 = 2$   
 Molarity of iodine solution =  $M_2 = 0.05\text{M}$   
 Volume of iodine solution =  $V_2 = 10.0 \text{ mL}$   
 No. of moles of iodine =  $n_2 = 1$

No	Initial burette reading	Final burette reading	Volume ( mL )
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10 mL

Substituting these values in molarity equation

$$(\text{Na}_2\text{S}_2\text{O}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{I}_2)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 10.0 \times 2}{1 \times 10} = 0.1\text{M}$$

Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  per  $\text{dm}^3$  = Molarity  $\times$  Molecular mass =  $0.1 \times 248 = 24.8 \text{ g}$

25 g sample of hypo contains pure  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = 24.8 \text{ g}$

$$\text{Percentage purity of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O} = \frac{\text{calculated amount of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O per dm}^3}{\text{Dissolved amount of } \text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O per dm}^3} \times 100$$

$$= \frac{24.8}{25} \times 100 = 99\%$$

**Result:** Purity of the given sample of hypo is 99%

## Exercise:

- Given solution contains 25 g mixture of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NaCl}$  dissolved per  $\text{dm}^3$ . Find out percentage composition of the mixture. (0.05M iodine solution is provided).
  - Standardize the given solution of iodine. How will you prepare 0.05-M solution from this solution? (0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  solution is provided).
  - Find out amount of  $\text{Na}_2\text{S}_2\text{O}_3$  dissolved per  $\text{dm}^3$  of the given solution. (0.1M iodine solution is provided).
- Hint:** Amount of  $\text{Na}_2\text{S}_2\text{O}_3$  per  $\text{dm}^3$  = Molarity  $\times$  Molecular mass.



## EXPERIMENT



Find out amount of  $\text{H}_2\text{O}_2$  per  $\text{dm}^3$  in the given sample of '10 volume' hydrogen peroxide using  $0.05 \text{ Na}_2\text{S}_2\text{O}_3 \text{ M}$  standard solution.

**Theory:** This is *Iodometric* titration. In these titrations 5% KI solution is added to aq. solution of  $\text{H}_2\text{O}_2$  which liberates equivalent amount of iodine. The liberated iodine is immediately titrated against standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  taken in the burette. The liberated  $\text{I}_2$  is equivalent to  $\text{H}_2\text{O}_2$ .

**Chemical Reactions:**



Mole ratio:  $\text{Na}_2\text{S}_2\text{O}_3, \text{I}_2 (\text{H}_2\text{O}_2) = 2:1$

Standard solution:  $0.05 \text{ Na}_2\text{S}_2\text{O}_3 \text{ M}$

Indicator: Starch solution

End point: Light blue colour

**Procedure:**

- 10 mL of given sample of  $\text{H}_2\text{O}_2$  was transferred to a 100 mL measuring flask and distilled water was added to make the volume 100 mL.
- 10 mL of this solution was taken in the iodine flask and about 1-2 g KI was added.
- Standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.
- Titration was repeated three or four times to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Molarity of solution  $\text{H}_2\text{O}_2 = M_1 = ?$

Volume of  $\text{H}_2\text{O}_2$  solution used  $= V_1 = 10.0 \text{ mL}$

No. of moles of  $\text{H}_2\text{O}_2 = n_1 = 1$

Molarity of  $\text{Na}_2\text{S}_2\text{O}_3$  solution  $= M_2 = 0.05 \text{ M}$

Volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used  $= V_2 = 10.0 \text{ mL}$

No. of moles of  $\text{Na}_2\text{S}_2\text{O}_3 = n_2 = 2$

Substituting the values in molarity equation

$$\begin{aligned} (\text{H}_2\text{O}_2) \quad \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} (\text{Na}_2\text{S}_2\text{O}_3) \\ M_1 &= \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 10.0 \times 1}{2 \times 10} = 0.0025 \text{ M} \end{aligned}$$

Hence, the molarity of the given solution  $= 0.0025 \text{ M}$

Amount of  $\text{H}_2\text{O}_2$  per  $\text{dm}^3 = \text{Molarity} \times \text{Molar mass of } \text{H}_2\text{O}_2 = 0.0025 \times 34 = 0.085 \text{ g per dm}^3$

As the solution was diluted 10 times, hence the amount of  $\text{H}_2\text{O}_2$  per  $\text{dm}^3$  in the given solution  $= 10 \times 0.085 \text{ g per dm}^3$

Amount of  $\text{H}_2\text{O}_2$  in the given solution per  $\text{dm}^3 = 8.5 \text{ g}$

**Result:**

Amount of  $\text{H}_2\text{O}_2$  in the given solution is  $8.5 \text{ g per dm}^3$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10 mL



# EXPERIMENT



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500 mL of given solution contains 7.9g of an alkali metal thiosulphate. Determine the atomic mass of the alkali metal (0.05M iodine solution is provided).

**Theory:** This is iodimetric redox titration. Iodine solution is titrated against sodium thiosulphate solution taken in the burette.

**Chemical Reactions:**



**Mole ratio:**  $\text{Na}_2\text{S}_2\text{O}_3 : \text{I}_2 = 2 : 1$

**Standard Solution:** 0.05 M Iodine solution.

**Indicator:** Starch solution

**End Point:** Light blue colour or just colour less.

**Procedure:**

- 10.0 mL iodine solution was taken in the iodine titration flask and 10.0 mL distilled water was added to it.
- Iodine solution was titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution taken in the burette until appearance of lemon yellow colour.
- 1 mL freshly prepared starch solution was added to the flask when lemon yellow colour appeared.
- This solution was again titrated until end point.
- Initial and final burette readings were noted.
- Volume used was found by subtracting initial burette reading from final burette reading.
- Experiment was repeated thrice to get the concordant readings

## OBSERVATIONS AND CALCULATIONS

Molarity of $\text{M}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution	$= M_1 = ?$
Volume of $\text{M}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ solution	$= V_1 = 10.0 \text{ mL}$
No. of mole of $\text{M}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	$= n_1 = 2$
Molarity of iodine solution	$= M_2 = 0.05\text{M}$
Volume of iodine solution	$= V_2 = 10.0 \text{ mL}$
No. of moles of iodine	$= n_2 = 1$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10 mL

Substituting these values in molarity equation

$$(\text{M}_2\text{SO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{I}_2)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 10.0 \times 2}{1 \times 10} = 0.1 \text{ M}$$

$$\text{Amount of } \text{M}_2\text{S}_2\text{O}_3 \text{ in } 500 \text{ mL} = 7.9 \text{ g}$$

$$\text{Amount of } \text{M}_2\text{S}_2\text{O}_3 \text{ in } 1 \text{ dm}^3 = \text{Molarity} \times \text{Molecular mass} = 7.9 \text{ g} / 500 \times 1000 = 15.8 \text{ g}$$

$$15.8 \text{ g per dm}^3 = 0.1 \times \text{Molecular mass.}$$

$$\text{Molecular mass of } \text{M}_2\text{S}_2\text{O}_3 = 15.8 / 0.1 = 158$$

$$\text{Molecular mass of } \text{M}_2\text{S}_2\text{O}_3 = (2M) + (32 \times 2 + 16 \times 3) = (2M + 112) = 158$$

$$2M = 158 - 112 = 46$$

$$M = 46 / 2 = 23 \text{ a.m.u.}$$

**Result:** Atomic mass of the Alkali metal is 23 a.m.u.

**Exercise:** Given solution contains 25g sample of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  dissolved per  $\text{dm}^3$ . Find out percentage purity of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  (0.05M iodine solution is provided).





## EXPERIMENT

# 12

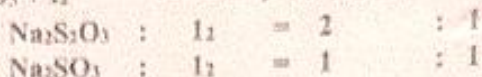
20 g sodium sulphite has been dissolved per  $\text{dm}^3$  of the given solution. Find out percentage purity of the sample. (0.01M iodine solution is provided).

**Theory:** Sodium sulphite is conveniently oxidized to sodium sulphate by iodine solution. But direct titration is not recommended. A known volume of sodium sulphite is added to a known volume of standard  $\text{I}_2$  solution where as unreacted iodine is titrated with standard sodium thiosulphate solution.

**Chemical Reactions:**



**Mole ratio:**



**Standard Solution:** 0.01 M Iodine solution.

**Indicator:** Starch solution

**End Point:** Light blue colour or just colour less.

**Procedure:**

- 20 mL solution of 0.1M iodine solution was taken in iodine flask and 10.0 mL of the given solution of sodium sulphite was added to it and stirred well.
- Unreacted iodine solution was titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution taken in the burette until appearance of lemon yellow colour.
- 1 mL freshly prepared starch solution was added to the flask when lemon yellow colour appeared.
- This solution was again titrated until end point.
- Initial and final burette readings were noted.
- Volume used was found by subtracting initial burette reading from final burette reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution =  $M_1$  = 0.1M  
 Volume of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  solution used =  $V_1$  = 20.0 mL  
 Molarity of iodine solution =  $M_2$  = 0.1M  
 No. of mole of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  =  $n_1$  = 2  
 No. of mole of  $\text{I}_2$  =  $n_2$  = 1  
 Volume of iodine used by 20.0 mL  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  =  $V_2$  = ?  
 Volume of iodine used by  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  can be calculated by using the Molarity equation

$$(\text{Na}_2\text{S}_2\text{O}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{I}_2)$$

$$V_2 = \frac{M_1 V_1 n_2}{n_1 M_2} = \frac{0.1 \times 20 \times 1}{2 \times 0.1} = 10 \text{ cm}^3$$

Hence volume of iodine solution which reacted with sodium sulphite =  $20 - 10 = 10$  mL.  
 Molarity of the sodium sulphite can be found as follows:

Molarity of  $\text{Na}_2\text{SO}_3$  =  $M_1$  = ?  
 Volume of  $\text{Na}_2\text{SO}_3$  =  $V_1$  = 10 mL  
 No. of moles of  $\text{Na}_2\text{SO}_3$  =  $n_1$  = 1  
 Molarity of  $\text{I}_2$  =  $M_2$  = 0.10M

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10 mL



Volume of  $I_2$  used =  $V_2$  = 10 ml  
 No. of moles of  $I_2$  = 1  
 Substituting the values in molarity equation

$$[Na_2SO_3] \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \quad (I_2)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.10 \times 10.0 \times 1}{1 \times 10} = 0.10 \text{ M}$$

Amount of sodium sulphite per dm<sup>3</sup> = Molarity  $\times$  Molecular mass =  $0.1 \times 126.04 = 12.6 \text{ g per dm}^3$   
 Amount of sodium sulphite per dm<sup>3</sup> dissolved in the given solution = 20 g per dm<sup>3</sup>

Percentage purity =  $\frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{12.6}{20.0} \times 100 = 63\%$

Result: Percentage purity of the given sample is 63 percent.

## Argentometry (Silver nitrate Titrations)

**Introduction:** These volumetric processes are based upon the formation of an insoluble precipitate when the two reacting solutions come together. The most important of such titrations involve the use of silver nitrate. When silver nitrate solution is added to a solution of a soluble chloride, bromide or an iodide, the halide is precipitated. For Example



The reaction is instantaneous and quantitative. When the halides are precipitated completely, the next drop of silver nitrate solution added is left unreacted and can be detected by means of a suitable indicator. Hence the soluble halides can be readily estimated by titrations with standard silver nitrate solution. Titrations which involve the use of standard silver nitrate solution are called silver nitrate titrations or argentometry. It can also be used in the estimation of cyanides, chlorates and iodates. Conversely, a standard solution of an alkali chloride may be used for the estimation of silver.

The end-point is determined with the help of either (i) precipitation indicator or (ii) adsorption indicator.

### Precipitation Indicator:

A common example of this is use of potassium chromate solution in the titration of chlorides by the silver nitrate solution in neutral medium. Potassium chromate forms a brick red precipitate with silver nitrate.



Therefore it is used as an internal indicator in titrations where silver nitrate is run from a burette. Silver chromate is more soluble than silver halide. Therefore the indicator does not react with silver nitrate unless the whole of halide has been precipitated as silver halide. 5% solution of pure potassium chromate is prepared in distilled water. About 5 drops of this solution is used at a time. The end point is the appearance of a faintly reddish tint in the precipitate or solution (mostly in precipitate). Excessive quantity of potassium chromate should be avoided; otherwise the intense yellow colour of the indicator will mask the end point.

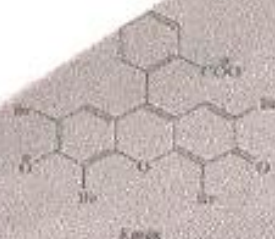
### Limitations of use of potassium chromate:

1. Potassium chromate can be used only in neutral solutions.  
 This is because (a): Silver chromate is soluble in acids, (b): Alkaline solution would react with the silver nitrate to form silver oxide.
2. Potassium chromate cannot be used for titration of iodides because of absorption phenomena and difficulty of distinguishing the colour change of potassium chromate.

**Adsorption Indicators:** Both fluorescein and dichloro fluorescein are suitable for the titration of chlorides. In both the cases the end point is reached when the white precipitate in the greenish yellow solution suddenly assumes a pronounced reddish tint.

### Preparation of Reagents:

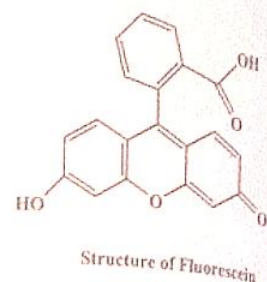
1. **Fluorescein solution:** Dissolve 0.2 g of fluorescein in 100 mL of 70% ethanol;





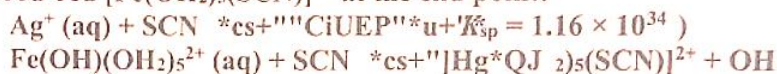
or dissolve 0.2g of sodium fluoresceinate in 100 mL of water.

- Eosin solution:** It is prepared by dissolving 0.1 g of eosin in 100 mL of 70% ethanol or by dissolving 0.1 g of the sodium salt in 100 mL of water.
- Potassium chromate solution:**
- 5 g potassium chromate is dissolved in 100 mL distilled water
- Silver nitrate standard solution (0.1M):** Silver nitrate is available in a state of high purity and can be weighed accurately. So its standard solution can be prepared by dissolving the calculated weight in water and then diluting the solution up to the calculated volume, for example, dissolve 16.98 g pure  $\text{AgNO}_3$  in 1 dm<sup>3</sup> flask containing 200 mL water and add more water to make the volume 1 dm<sup>3</sup>. This would be 0.1M solution.
- KCNS Standard Solution(0.1M):** Dissolve accurately weighed 9.7 g KCNS in 400 mL of distilled water in a 1000 mL flask and add more distilled water to make up the volume up to the mark. This would be 0.1M solution.
- NaCl Standard Solution (0.1M):** Sodium chloride is slightly hygroscopic, therefore, it should be dried at 250-300°C for 2-3 hours in an electric oven and cool it in a covered vessel in a desiccators. Weigh out accurately 5.85 g dried NaCl and dissolve it in distilled water in a 1000 mL flask. Add more water to make up the volume 1 dm<sup>3</sup>



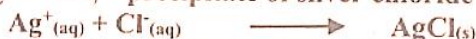
**Argentometric Methods of Titrations:** Three methods are commonly used in Argentometry.

- Volhard method:** This method involves the addition of excess silver nitrate to the analyte; the silver chloride is filtered, and the remaining silver nitrate is titrated against thiocyanate, with iron(III) as an indicator which forms blood-red  $[\text{Fe}(\text{OH}_2)_5(\text{SCN})]^{2+}$  at the end point:



## 2. Mohr method

This method determines the chloride ion concentration of a solution by titration with silver nitrate. As the silver nitrate solution is slowly added, a precipitate of silver chloride forms.

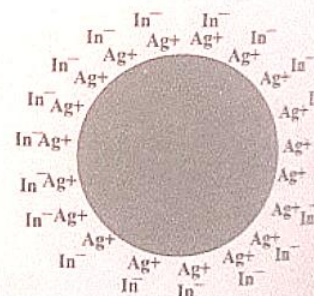


The indicator used is dilute potassium chromate solution. When all the chloride ions have reacted, any excess silver nitrate added will react with chromate ions to form a red-brown precipitate of silver chromate. This is the *chromate method*.



The solution should be near neutral, because silver hydroxide forms at high pH, while the chromate forms  $\text{H}_2\text{CrO}_4$  at low pH, reducing the concentration of chromate ions, and delaying the formation of the precipitate. Carbonates and phosphates precipitate with silver, and should be absent to prevent inaccurate results.

- Fajan's method:** In this method, dichlorofluorescein is used as an indicator; the end-point is marked by the green suspension turning pink. Prior to the end-point of the titration, chloride ions remain in excess. They adsorb on the  $\text{AgCl}$  surface, imparting a negative charge to the particles. Past the end-point, excess silver(I) ions adsorb on the  $\text{AgCl}$  surface, imparting a positive charge. Anionic dyes such as dichlorofluorescein are attracted to the particles, and undergo a colour change upon adsorption, representing the end-point. Eosin (tetrabromofluorescein) is suitable for titrating against bromide, iodide, and thiocyanate anions, giving a sharper end-point than dichlorofluorescein. It is not suitable for titrating against chloride anions because it binds to  $\text{AgCl}$  more strongly than chloride.





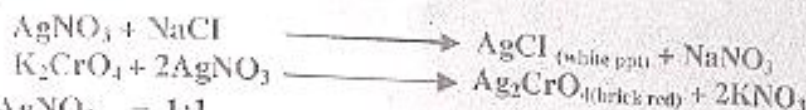
## EXPERIMENT

1

1g NaCl is dissolved in 250 mL of the given solution. Find out percentage purity of NaCl using Mohr's method. 0.05 M  $\text{AgNO}_3$  is provided.

Theory: sodium chloride solution is titrated against standard solution of  $\text{AgNO}_3$  using  $\text{K}_2\text{CrO}_4$  as an indicator in early neutral solution.

Chemical Reactions:



Mole ratio:  $\text{NaCl} : \text{AgNO}_3 = 1:1$

Standard Solution: 0.1 M  $\text{AgNO}_3$

Indicator:  $\text{K}_2\text{CrO}_4$

End Point: Brick red ppt.

Procedure:

1. 10 mL solution of NaCl solution was taken in the flask and 1-2 drops of  $\text{K}_2\text{CrO}_4$  were added as indicator.
2. This solution was titrated against standard solution of  $\text{AgNO}_3$  until end point.
3. Initial and final burette readings were noted.
4. Volume used was found by subtracting initial burette reading from final burette reading.
5. Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of NaCl solution	$= M_1$	$= ?$
Volume of NaCl taken in the flask	$= V_1$	$= 10.0 \text{ mL}$
No. of mole of NaCl	$= n_1$	$= 1$
Molarity of $\text{AgNO}_3$ solution	$= M_2$	$= 0.1 \text{ M}$
No. of mole of $\text{AgNO}_3$	$= n_2$	$= 1$
Volume of $\text{AgNO}_3$ used	$= V_2$	$= 10.0 \text{ mL}$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.1	31.1	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{NaCl}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.10 \times 10.0 \times 1}{1 \times 10} = 0.1 \text{ M}$$

$$\text{Amount of NaCl per dm}^3 = \text{Molarity} \times \text{Molecular mass} = 0.1 \times 58.5 = 5.85 \text{ g per dm}^3$$

$$\text{Amount of NaCl dissolved in 250 mL of the given solution} = 2.0 \text{ g}$$

$$\text{Amount of NaCl dissolved per dm}^3 = \frac{2}{250} \times 1000 = 8.0 \text{ g}$$

$$\text{Percentage purity} = \frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{5.85}{8.0} \times 100 = 73.125\%$$

Result: Percentage purity of the given sample is 73.125 percent.

Exercise:

1. 20 g  $\text{AgNO}_3$  has been dissolved per  $\text{dm}^3$  of the given solution. Determine percentage purity of  $\text{AgNO}_3$ . 0.1M NaCl standard solution is provided.
2. Determine the amount of  $\text{Cl}^-$  ion in the given sample solution of NaCl. 0.1M  $\text{AgNO}_3$  standard solution is provided.

Hints: Find out molarity of NaCl by using  $\text{AgNO}_3$  as standard and  $\text{K}_2\text{CrO}_4$  as indicator. Let the molarity of NaCl is 0.1M. Calculate the amount of  $\text{Cl}^-$  ion by using the equation.

$$\text{Amount of } \text{Cl}^- \text{ ion per dm}^3 = \text{Molarity} \times \text{Ionic mass of } \text{Cl}^- \text{ ion} = 0.1 \times 35.5 = 3.5 \text{ g per dm}^3$$



# EXPERIMENT

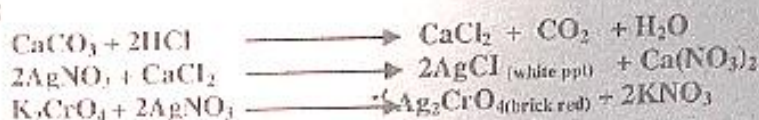


## 2

Determine amount of HCl in the commercial sample by Mohr's method. 0.05 M  $\text{AgNO}_3$  is provided.

**Theory:** Theory: Molarity of commercial HCl is about 10-11M. A diluted HCl (~ 0.1M) solution is neutralized with  $\text{CaCO}_3$  and resulting  $\text{CaCl}_2$  is titrated against standard  $\text{AgNO}_3$  solution. Molarity of HCl is then calculated

**Chemical Reactions:**



Mole ratio:  $\text{CaCl}_2 : \text{AgNO}_3 = 1:2$

Mole ratio:  $\text{CaCl}_2 : \text{HCl} = 1:2$

Standard Solution: 0.1 M  $\text{AgNO}_3$

Indicator:  $\text{K}_2\text{CrO}_4$

End Point: Brick red ppt.

**Procedure:**

- 10 mL solution of commercial HCl was taken in 100 mL flask and distilled water was added to make up the volume 100 mL. Solid  $\text{CaCO}_3$  was added to the solution until the effervescence ceases.
- 10 mL solution of this solution was taken in the titration flask and 1-2 drops of  $\text{K}_2\text{CrO}_4$  were added as indicator.
- This solution was titrated against standard solution of  $\text{AgNO}_3$  until end point.
- Initial and final burette readings were noted.
- Volume used was found by subtracting initial burette reading from final burette reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of  $\text{CaCl}_2$  solution

$$= M_1 = ?$$

Volume of  $\text{CaCl}_2$  taken in the flask

$$= V_1 = 10.0 \text{ mL}$$

No. of mole of  $\text{CaCl}_2$

$$= n_1 = 1$$

Molarity of  $\text{AgNO}_3$  solution

$$= M_2 = 0.1 \text{ M}$$

No. of mole of  $\text{AgNO}_3$

$$= n_2 = 2$$

Volume of  $\text{AgNO}_3$  used

$$= V_2 = 10.0 \text{ mL}$$

Substituting these values in molarity equation

$$(\text{CaCl}_2) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.10 \times 10.0 \times 1}{2 \times 10} = 0.05 \text{ M}$$

Molarity of  $\text{CaCl}_2 = 0.05 \text{ M}$

Mole ratio between  $\text{CaCl}_2$  and  $\text{HCl} = 2:1$

Hence the molarity of HCl =  $0.05 \text{ M} \times 2 = 0.1 \text{ M}$

Amount of HCl per  $\text{dm}^3 = \text{Molarity} \times \text{Molecular mass} = 0.1 \times 36.5 = 3.65 \text{ g per dm}^3$

As the commercial HCl was diluted 10 times, hence,

Amount of HCl dissolved per  $\text{dm}^3 = 3.65 \times 10 = 36.5 \text{ g per dm}^3$

**Result:** The given HCl sample contains 36.5 g per  $\text{dm}^3$  HCl.



# EXPERIMENT



## 3

The given solution contains 0.6935 g pure  $\text{MCl}_2$  dissolved in 500 mL. Determine the atomic mass of 'M'. 0.025 M  $\text{AgNO}_3$  solution is provided.

**Theory:** Halides can be estimated by titrating their neutral solutions with standard  $\text{AgNO}_3$  solution using  $\text{K}_2\text{CrO}_4$  solution as indicator.

**Chemical reactions:**



**Mole ratio:**  $\text{MCl}_2 : \text{AgNO}_3 = 1:2$

**Standard Solution:** 0.025 M  $\text{AgNO}_3$

**Indicator:**  $\text{K}_2\text{CrO}_4$

**End Point:** Brick red ppt.

**Procedure:**

- 10 mL solution of  $\text{MCl}_2$  was taken in the titration flask and 1-2 drops of  $\text{K}_2\text{CrO}_4$  were added as indicator.
- This solution was titrated against standard solution of  $\text{AgNO}_3$  until end point.
- Initial and final burette readings were noted.
- Volume used was found by subtracting initial burette reading from final burette reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of $\text{MCl}_2$ solution	=	$M_1 = ?$
Volume of $\text{MCl}_2$ taken in the flask	=	$V_1 = 10.0 \text{ mL}$
No. of mole of $\text{MCl}_2$	=	$n_1 = 1$
Molarity of $\text{AgNO}_3$ solution	=	$M_2 = 0.025 \text{ M}$
No. of mole of $\text{AgNO}_3$	=	$n_2 = 2$
Volume of $\text{AgNO}_3$ used	=	$V_2 = 10.0 \text{ mL}$

No	Initial reading	Final reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

$$(\text{MCl}_2) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.025 \times 10.0 \times 1}{2 \times 10.0} = 0.0125 \text{ M}$$

Molarity of $\text{MCl}_2$	=	0.0125 M
Amount of $\text{MCl}_2$ dissolved in 500 mL	=	0.6935 g
Amount of $\text{MCl}_2$ dissolved in 1000 mL	=	1.387 g
Amount of $\text{MCl}_2$ per $\text{dm}^3$ = Molarity x Molecular mass	=	$0.0125 \times (M + 71) = 1.387 \text{ g}$
	=	$1.387 / 0.0125 = 110.96 \text{ g}$
	=	$(M + 71)$
	=	$M = 110.96 - 71 = 39.96 \text{ g per mol}$

**Result:** The atomic mass of 'M' is 39.96 g per mol



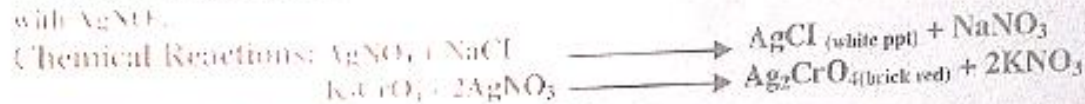
## EXPERIMENT



4

12 g mixture of NaCl and  $\text{KNO}_3$  is dissolved per  $\text{dm}^3$  of the given solution. Determine the percentage of the mixture.  $0.025\text{M AgNO}_3$  is provided.

Theory: This is Argentometric titration. Mohr's method can be used in this titration as  $\text{KNO}_3$  does not react with  $\text{AgNO}_3$ .



Molar ratio:  $\text{NaCl} : \text{AgNO}_3 = 1:1$

Standard Solution:  $0.025\text{M AgNO}_3$

Indicator:  $\text{K}_2\text{CrO}_4$

End Point: Brick red ppt.

Procedure:

1. 10 mL solution of NaCl and  $\text{KNO}_3$  solution was taken in the flask and 1-2 drops of  $\text{K}_2\text{CrO}_4$  were added as indicator.
2. This solution was titrated against standard solution of  $\text{AgNO}_3$  until end point.
3. Initial and final burette readings were noted.
4. Volume used was found by subtracting initial burette reading from final burette reading.
5. Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Molarity of NaCl solution	=	$M_1 = ?$
Volume of NaCl taken in the flask	=	$V_1 = 10.0\text{ mL}$
No. of mole of NaCl	=	$n_1 = 1$
Molarity of $\text{AgNO}_3$ solution	=	$M_2 = 0.025\text{ M}$
No. of mole of $\text{AgNO}_3$	=	$n_2 = 1$
Volume of $\text{AgNO}_3$ used	=	$V_2 = 10.0\text{ mL}$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.0	30.0	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{NaCl}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.025 \times 10.0 \times 1}{1 \times 10} = 0.025\text{M}$$

Amount of NaCl per  $\text{dm}^3$  = Molarity  $\times$  Molecular mass =  $0.025 \times 58.5 = 1.4625\text{ g per dm}^3$

Amount of NaCl and  $\text{KNO}_3$  dissolved per  $\text{dm}^3$  of the given solution = 12.0 g

$$\text{Percentage of NaCl} = \frac{\text{Calculate amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{1.4625}{12.0} \times 100 = 12.19\%$$

$$\text{Percentage of KNO}_3 = 100 - 12.19 = 87.81\%$$

Result: The given mixture consists of 12.19% NaCl and 87.81%  $\text{KNO}_3$

Exercise:

1. 10 g of commercial sodium chloride is dissolved per  $\text{dm}^3$  in the given solution. Find the percentage impurity of the sample
2. 12 g mixture of NaCl and  $\text{Na}_2\text{SO}_4$  is dissolved per  $\text{dm}^3$  in the given solution. Determine the percentage composition of the mixture using  $0.025\text{M AgNO}_3$



## EXPERIMENT



5

Determine the amount per dm<sup>3</sup> of HNO<sub>3</sub> and HCl in the given solution. 0.1M NaOH and 0.05M AgNO<sub>3</sub> is provided.

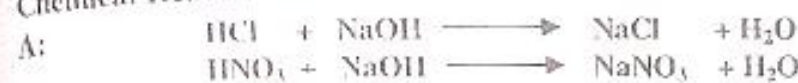
Theory: This is two steps titration. Total acid strength is determined by titrating the given solution with standard NaOH solution in the first step. Acid solution is then neutralized with CaCO<sub>3</sub> and resulting solution is titrated with standard AgNO<sub>3</sub> using potassium chromate solution as indicator. Concentration of HNO<sub>3</sub> is calculated by difference method.



Mole ratio: AgNO<sub>3</sub> : CaCl<sub>2</sub> = 2:1

Titration A:

Chemical Reactions



Mole ratio: Acids : NaOH = 1:1

Indicator : Phenolphthalein

End point : Very light pink colour

Procedure:

- 10.0 ml. of standard NaOH solution was taken in the titration flask with pipette and 1-2 drops of phenolphthalein indicator were added to it.
- This solution was titrated against given solution of acids taken in the burette till end point.
- Volume of acid used was found by subtracting initial burette reading from final burette reading.
- Titration was repeated thrice to get the concordant readings

## OBSERVATIONS AND CALCULATIONS

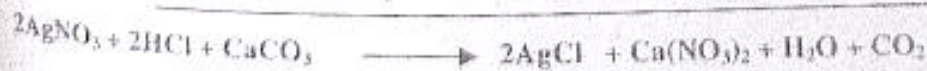
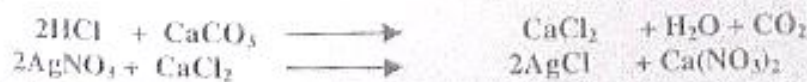
Volume of NaOH	= V <sub>1</sub>	=	10.0 mL
Molarity of NaOH	= M <sub>1</sub>	=	0.1M
No. of moles of NaOH	= n <sub>1</sub>	=	1
Volume of acid solution	= V <sub>2</sub>	=	10.0 mL
Molarity of acid solution	= M <sub>2</sub>	=	?
No. of moles of oxalic acid	= n <sub>2</sub>	=	1

Substituting these values in molarity equation

$$\begin{aligned} (\text{NaOH}) \quad \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} \quad (\text{Oxalic Acid}) \\ M_2 &= \frac{M_1 V_1}{n_1} \times \frac{n_2}{V_2} = \frac{0.1 \times 10 \times 1}{1 \times 10} = 0.1 \end{aligned}$$

Molarity with respect to both acids = 0.1M

Titration B:



Mole ratio: AgNO<sub>3</sub> : HCl(converted to CaCl<sub>2</sub>) = 1:1

Standard Solution: 0.05 M AgNO<sub>3</sub>

Indicator: K<sub>2</sub>CrO<sub>4</sub>

End Point: Brick red ppt.

No	Initial burette reading	Final burette reading	Volume ( mL )
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.0	30.0	10.0

Volume used = 10.0 mL



### Procedure:

1. 10 mL solution of given acids was taken in the titration flask. Solid  $\text{CaCO}_3$  was added pinch by pinch to the solution until the effervescence ceases and some solid remained undissolved.
2. 10 mL solution of this solution was taken in the titration flask and 1-2 drops of  $\text{K}_2\text{CrO}_4$  were added as indicator.
3. This solution was titrated against standard solution of  $\text{AgNO}_3$  until end point.
4. Initial and final burette readings were noted.
5. Volume used was found by subtracting initial burette reading from final burette reading.
6. Experiment was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Molarity of HCl solution (converted to  $\text{CaCl}_2$ ) =  $M_1$  = ?  
 Volume of HCl solution (converted to  $\text{CaCl}_2$ ) =  $V_1$  = 10.0 mL

No. of mole of HCl solution (converted to  $\text{CaCl}_2$ ) =  $n_1$  = 1  
 Molarity of  $\text{AgNO}_3$  solution =  $M_2$  = 0.05M  
 No. of mole of  $\text{AgNO}_3$  =  $n_2$  = 1  
 Volume of  $\text{AgNO}_3$  used =  $V_2$  = 10.0 mL  
 Substituting these values in molarity equation

$$(\text{CaCl}_2) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.05 \times 10.0 \times 1}{1 \times 10} = 0.05\text{M}$$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.0	30.0	10.0

Volume used = 10.0 mL

Molarity of HCl solution (converted to  $\text{CaCl}_2$ ) = 0.05M  
 Molarity with respect to  $\text{HNO}_3$  and HCl = 0.10M  
 Molarity with respect to HCl = 0.05M  
 Molarity with respect to  $\text{HNO}_3$  = 0.10M — 0.05M = 0.05M  
 Amount of HCl per  $\text{dm}^3$  = Molarity x Molar mass = 0.05M x 36.5 g/mol = 1.82 g per  $\text{dm}^3$   
 Amount of  $\text{HNO}_3$  per  $\text{dm}^3$  = Molarity x Molar mass = 0.05M x 63.01 g/mol = 3.15 g per  $\text{dm}^3$   
 Result: The given solution contains 1.82 g per  $\text{dm}^3$  HCl and 3.15 g per  $\text{dm}^3$   $\text{HNO}_3$

### EXPERIMENT



# 6

Standardize the given solution of  $\text{AgNO}_3$ . 0.1M KCNS is provided.

**Theory:**  $\text{AgNO}_3$  is titrated with standard KCNS solution using ferric alum as an indicator. When all added  $\text{AgNO}_3$  is consumed by KCNS, a drop of  $\text{AgNO}_3$  reacts with  $\text{Fe}^{+++}$  ions to give the reddish pink ppt, which is end point.

#### Chemical Reactions:



Mole ratio:  $\text{AgNO}_3$  : KCNS = 1 : 1

Indicator: Ferric alum

End point: Permanent reddish tinge

#### Procedure:

1. 10 mL of the given  $\text{AgNO}_3$  solution was taken in the titration flask and 1 mL solution of ferric alum was added to it



- This solution was titrated against KCNS taken in the burette until the end point reached.
- The experiment was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Molarity of  $\text{AgNO}_3$  solution =  $M_1 = ?$   
 Volume of  $\text{AgNO}_3$  taken in the flask =  $V_1 = 10.0 \text{ mL}$   
 No. of mole of  $\text{AgNO}_3$  =  $n_1 = 1$   
 Molarity of KCNS solution =  $M_2 = 0.1 \text{ M}$   
 No. of mole of KCNS =  $n_2 = 1$   
 Volume of KCNS used =  $V_2 = 10.0 \text{ mL}$   
 Substituting these values in molarity equation

$$(\text{AgNO}_3) \quad \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KCNS})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 10} = 0.1 \text{ M}$$

No	Initial burette reading	Final burette reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.0	30.0	10.0

Volume used = 10.0 mL

Result: The molarity of given  $\text{AgNO}_3$  is 0.10M

### EXPERIMENT

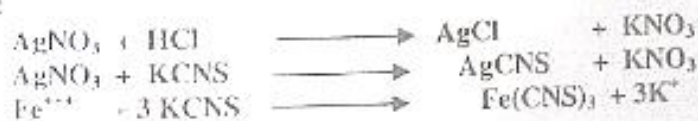


# 7

Determine the amount of HCl dissolved per  $\text{dm}^3$  in the given solution. 0.10M  $\text{AgNO}_3$  and 0.10M KCNS solutions are provided.

**Theory:** Determination of halide ions in acidic media make use of Volhard's method. Volhard's method involves the addition of excess silver nitrate to the analyte; the silver chloride is filtered, and the remaining silver nitrate is titrated against thiocyanate, with iron(III) as an indicator which forms blood-red  $[\text{Fe}(\text{OH})_2(\text{SCN})]^{+}$  at the end point.

**Chemical Reactions:**



Mole ratio:  $\text{AgNO}_3 : \text{KCNS} = 1 : 1$

Indicator: Ferric alum

End point: Permanent reddish tinge

**Procedure:**

- 1 mL of the given HCl was diluted to 100 mL. 10 mL of the diluted HCl was taken in a flask.
- 2 mL conc.  $\text{HNO}_3$  and 20 mL of 0.10 M  $\text{AgNO}_3$  solution were added to the flask and flask was wrapped with black paper.
- Flask was warmed on a water bath to complete precipitation. Ppt. was filtered off and washed with water three times.
- Filtrate and washings were collected in a titration flask.
- About 1 mL of 2% ferric alum solution was added to the titration flask as indicator. The contents were titrated against standard KCNS solution taken in the burette till the end point.
- Titration was repeated thrice to get the concordant readings.



## OBSERVATIONS AND CALCULATIONS

Volume of HCl solution taken	= 10.0 mL
Molarity of AgNO <sub>3</sub> solution	= M <sub>1</sub> = 0.10M
Volume of AgNO <sub>3</sub> added to HCl solution	= V <sub>x</sub> = 20.0 mL
No. of mole of AgNO <sub>3</sub>	= n <sub>1</sub> = 1
Molarity of KCNS solution	= M <sub>2</sub> = 0.1M
No. of mole of KCNS	= n <sub>2</sub> = 1
Volume of KCNS used	= V <sub>2</sub> = 10.0 mL
Volume of AgNO <sub>3</sub>	= V <sub>1</sub> = ?

No	Initial reading	Final reading	Volume of KCNS (mL)
1	0.0	10.0	10.0
2	10.0	21.1	10.1
3	20.0	30.0	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KCNS})$$

$$V_1 = \frac{M_2 V_2 n_1}{n_2 M_1} = \frac{0.10 \times 10.0 \times 1}{1 \times 0.10} = 10 \text{ cm}^3$$

Hence the volume of unreacted AgNO <sub>3</sub>	= 10 mL	
Volume of AgNO <sub>3</sub> that reacted with HCl	= 20.0 mL	10.0 mL = V <sub>1</sub> = 10.0 mL
Molarity of AgNO <sub>3</sub>	= M <sub>1</sub>	= 0.10M
No. of mole of AgNO <sub>3</sub>	= n <sub>1</sub>	= 1
Volume of HCl solution taken	= V <sub>2</sub> = 10.0 mL	
No. of mole of AgNO <sub>3</sub>	= n <sub>2</sub> = 1	
Molarity of HCl solution taken	= M <sub>2</sub> = ?	

Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{HCl})$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.10 \times 10.0 \times 1}{1 \times 10} = 0.10 \text{ M}$$

Molarity of diluted HCl solution = 0.10M

As 1 mL HCl solution was diluted to 100 mL (100 times), Hence molarity of given HCl = 0.10 x 100 = 10M

Amount of HCl per dm<sup>3</sup> = Molarity x Molar mass = 10M x 36.5 = 365 g per dm<sup>3</sup>

**Result:** The given solution of contains 365 g per dm<sup>3</sup> HCl.

## EXPERIMENT

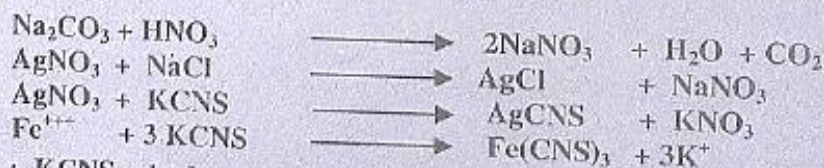


# 8

The given solution contains 25 g soda ash per dm<sup>3</sup>. Determine the percentage of NaCl in soda ash. 0.10M AgNO<sub>3</sub> and 0.10M KCNS solutions are provided.

**Theory:** Soda ash contains NaCl as impurity. NaCl can be Determined acidic media by Volhard's method. Volhard's method involves the addition of excess silver nitrate to the analyte; the silver chloride is filtered, and the remaining silver nitrate is titrated against thiocyanate, with iron(III) as an indicator which forms blood-red [Fe(OH)<sub>2</sub>(SCN)]<sup>2+</sup> at the end point. Sample solution is treated with HNO<sub>3</sub> to make the medium acidic.

**Chemical Reactions:**



Mole ration: AgNO<sub>3</sub> : KCNS = 1 : 1

AgNO<sub>3</sub> : NaCl = 1 : 1

Indicator: Ferric alum

End point: Permanent reddish tinge



**Procedure:**

1. 40 mL of the given solution was taken in a flask and conc.  $\text{HNO}_3$  was added to it until effervescence ceased.
2. 2 mL conc.  $\text{HNO}_3$  and 20 mL of 0.10M  $\text{AgNO}_3$  solution were added to the flask and flask was wrapped with black paper.
3. Flask was warmed on a water bath to complete precipitation. Ppt. was filtered off and washed with water three times.
4. Filtrate and washings were collected in a titration flask.
5. About 1 mL of 2% ferric alum solution was added to the titration flask as indicator. The contents were titrated against standard KCNS solution taken in the burette till the end point.
6. Titration was repeated thrice to get the concordant readings.

**OBSERVATIONS AND CALCULATIONS**

Volume of soda ash solution taken	= 40.0 mL
Molarity of $\text{AgNO}_3$ solution	= $M_1$ = 0.10M
Volume of $\text{AgNO}_3$ added to soda ash solution	= $V_1$ = 20.0 mL
No. of mole of $\text{AgNO}_3$	= $n_1$ = 1
Molarity of KCNS solution	= $M_2$ = 0.1M
No. of mole of KCNS	= $n_2$ = 1
Volume of KCNS used	= $V_2$ = 10.0 mL
Volume of $\text{AgNO}_3$	= $V_1$ ?

N	Initial reading	Final reading	Volume of KCNS (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KCNS})$$

$$V_1 = \frac{M_2 V_2 n_1}{n_2 M_1} = \frac{0.10 \times 10.0 \times 1}{1 \times 0.10} = 10 \text{ mL}$$

Hence the volume of unreacted  $\text{AgNO}_3$  = 10 mLVolume of  $\text{AgNO}_3$  that reacted with NaCl = 20.0 mL - 10.0 mL =  $V_1$  = 10.0 mLMolarity of  $\text{AgNO}_3$  =  $M_1$  = 0.10MNo. of mole of  $\text{AgNO}_3$  =  $n_1$  = 1Volume of soda ash (NaCl) solution taken =  $V_2$  = 40.0 mLNo. of mole of NaCl =  $n_2$  = 1Molarity of NaCl solution taken =  $M_2$  = ?

Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{NaCl})$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.10 \times 10.0 \times 1}{1 \times 40} = 0.025 \text{ M}$$

Molarity of diluted NaCl solution = 0.025 M

Amount of NaCl per  $\text{dm}^3$  = Molarity  $\times$  Molar mass =  $0.025 \times 58.5 = 1.4625 \text{ g per dm}^3$ Amount of soda ash dissolved per  $\text{dm}^3$  = 25 gPercentage of NaCl in the soda ash =  $\frac{\text{Mass of NaCl per dm}^3}{\text{Mass of soda ash per dm}^3} \times 100 = \frac{1.4625}{25} \times 100 = 5.85\%$ **Result:** The given solution contains 5.85% NaCl**Exercise:** Find out percentage of NaCl in a sample of baking soda using 0.10M  $\text{AgNO}_3$  and 0.10M KCNS solutions.



# EXPERIMENT

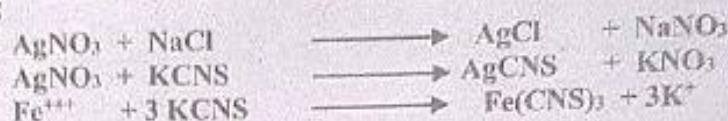


9

Find out the percentage composition of the given mixture of NaCl and  $\text{HNO}_3$ , 10 g of which has been dissolved per  $\text{dm}^3$ . 0.10 M  $\text{AgNO}_3$  and 0.10M KCNS solutions are provided

**Theory:** NaCl can be determined in acidic media by Volhard's method. Volhard's method involves the addition of excess silver nitrate to the analyte; the silver chloride is filtered, and the remaining silver nitrate is titrated against thiocyanate, with iron(III) as an indicator which forms blood-red  $[\text{Fe}(\text{OH})_2(\text{SCN})]^{2+}$  at the end point. Sample solution is treated with  $\text{HNO}_3$  to make the medium acidic.

**Chemical Reactions:**



**Mole ratio:**  $\text{AgNO}_3 : \text{KCNS} = 1 : 1$

$\text{AgNO}_3 : \text{NaCl} = 1 : 1$

**Indicator:** Ferric alum

**End point:** Permanent reddish tinge

**Procedure:**

- 20 mL of the given solution was taken in a flask and conc.  $\text{HNO}_3$  was added to it until effervescence ceased.
- 2 mL conc.  $\text{HNO}_3$  and 20 mL of 0.10M  $\text{AgNO}_3$  solution were added to the flask and flask was wrapped with black paper.
- Flask was warmed on a water bath to complete precipitation. Ppt. was filtered off and washed with water three times.
- Filtrate and washings were collected in a titration flask.
- About 1 mL of 2% ferric alum solution was added to the titration flask as indicator. The contents were titrated against standard KCNS solution taken in the burette till the end point.
- Titration was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of soda ash solution taken = 20.0 mL  
 Molarity of  $\text{AgNO}_3$  solution =  $M_1 = 0.10\text{M}$   
 Volume of  $\text{AgNO}_3$  added to soda ash solution =  $V = 20.0 \text{ mL}$   
 No. of mole of  $\text{AgNO}_3$  =  $n_1 = 1$   
 Molarity of KCNS solution =  $M_2 = 0.1\text{M}$   
 No. of mole of KCNS =  $n_2 = 1$   
 Volume of KCNS used =  $V_2 = 10.0 \text{ mL}$   
 Volume of  $\text{AgNO}_3$  =  $V_1 = ?$

Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KCNS})$$

$$V_1 = \frac{M_2 V_2 n_1}{n_2 M_1} = \frac{0.10 \times 10.0 \times 1}{1 \times 0.10} = 10 \text{ cm}^3$$

Hence the volume of unreacted  $\text{AgNO}_3$  = 10 mL

Volume of  $\text{AgNO}_3$  that reacted with NaCl = 20.0 mL - 10.0 mL =  $V_1 = 10.0 \text{ mL}$

Molarity of  $\text{AgNO}_3$  =  $M_1 = 0.10\text{M}$

No	Initial reading	Final reading	Volume of KCNS mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL



No. of mole of  $\text{AgNO}_3$   
 Volume of soda ash ( $\text{NaCl}$ ) solution taken  $= n_1 = 1$   
 $= V_2 = 20.0 \text{ mL}$   
 No. of mole of  $\text{NaCl}$   $= n_2 = 1$   
 Molarity of  $\text{NaCl}$  solution taken  $= M_2 = ?$   
 Substituting these values in molarity equation  
 $(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{NaCl})$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.10 \times 10.0 \times 1}{1 \times 20} = 0.05 \text{ M}$$

Molarity of  $\text{NaCl}$  solution

Amount of  $\text{NaCl}$  per  $\text{dm}^3$

Amount of  $\text{NaCl}$  and  $\text{HNO}_3$  dissolved per  $\text{dm}^3$

$$= 0.05 \text{ M}$$

$$= \text{Molarity} \times \text{Molar mass} = 0.05 \times 58.5 = 2.925 \text{ g per dm}^3$$

$$= 10 \text{ g}$$

Percentage of  $\text{NaCl}$  in the mixture

$$= 29.25\%$$

$$= \frac{\text{Mass of NaCl per dm}^3}{\text{Mass of soda ash per dm}^3} \times 100 = \frac{2.925}{10} \times 100$$

Percentage of  $\text{HNO}_3$  in the mixture  $= 100 - 29.25 = 70.75\%$

Result: The given solution contains 29.25%  $\text{NaCl}$  and 70.75%  $\text{HNO}_3$

## EXPERIMENT

10

5.15 g of an alkali metal bromide is dissolved per  $\text{dm}^3$  in the given solution. Determine atomic mass of the metal. 0.05M  $\text{AgNO}_3$  and 0.05M  $\text{KCNS}$  solutions are provided.

**Theory:** Bromides can be determined in acidic media by Volhard's method. Volhard's method involves the addition of excess silver nitrate to the analyte; the silver chloride is filtered, and the remaining silver nitrate is titrated against thiocyanate, with iron(III) as an indicator which forms blood-red  $[\text{Fe}(\text{OH})_2(\text{SCN})]^{2+}$  at the end point. Sample solution is treated with  $\text{HNO}_3$  to make the medium acidic.

**Chemical Reactions:**



**Standard solutions:** 0.05 M  $\text{KCNS}$  and 0.1M  $\text{AgNO}_3$

**Mole ratio:**  $\text{AgNO}_3 : \text{KCNS} = 1 : 1$

$\text{AgNO}_3 : \text{MBr} = 1 : 1$

**Indicator:** Ferric alum

**End point:** Permanent reddish tinge

**Procedure:**

- 20 mL of the  $\text{MBr}$  solution was taken in a flask and conc.  $\text{HNO}_3$  was added to it until effervescence ceased.
- 2 mL conc.  $\text{HNO}_3$  and 40 mL of 0.010M  $\text{AgNO}_3$  solution were added to the flask and flask was wrapped with black paper.
- Flask was warmed on a water bath to complete precipitation. Ppt. was filtered off and washed with water three times.
- Filtrate and washings were collected in a titration flask.
- About 1 mL of 2% ferric alum solution was added to the titration flask as indicator. The contents were titrated against standard  $\text{KCNS}$  solution taken in the burette till the end point.



6. Titration was repeated thrice to get the concordant readings

### OBSERVATIONS AND CALCULATIONS

Volume of MBr solution taken = 20.0 mL  
 Molarity of  $\text{AgNO}_3$  solution =  $M_1 = 0.10\text{M}$   
 Volume of  $\text{AgNO}_3$  added to soda ash solution =  $V = 40.0\text{ mL}$   
 No. of mole of  $\text{AgNO}_3$  =  $n_1 = 1$   
 Molarity of KCNS solution =  $M_2 = 0.05\text{M}$   
 No. of mole of KCNS =  $n_2 = 1$   
 Volume of KCNS used =  $V_2 = 20.0\text{ mL}$   
 Volume of  $\text{AgNO}_3$  unreacted =  $V_1 = ?$   
 Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KCNS})$$

$$V_1 = \frac{M_2 V_2 n_1}{n_2 M_1} = \frac{0.05 \times 20.0 \times 1}{1 \times 0.05} = 20\text{cm}^3$$

Hence the volume of unreacted  $\text{AgNO}_3$  = 20 mL  
 Volume of  $\text{AgNO}_3$  that reacted with MBr =  $40.0\text{ mL} - 20.0\text{ mL} = V_1 = 20.0\text{ mL}$   
 Molarity of  $\text{AgNO}_3$  =  $M_1 = 0.1\text{M}$   
 No. of mole of  $\text{AgNO}_3$  =  $n_1 = 1$   
 Volume of MBr solution taken =  $V_2 = 40.0\text{ mL}$   
 No. of mole of MBr =  $n_2 = 1$   
 Molarity of MBr solution taken =  $M_2 = ?$   
 Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{MBr})$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.1 \times 20.0 \times 1}{1 \times 40} = 0.05$$

Molarity of MBr solution = 0.05 M

Amount of MBr per  $\text{dm}^3 = 5.15\text{ g per dm}^3 = \text{Molarity} \times \text{Molar mass} = 0.05 \times (M+80)$

$$M+80 = \frac{5.15}{0.05} = 103$$

$$M = 103 - 80 = 23\text{ g per mole}$$

Result: Atomic mass of the alkali metal is 23 a.m.u.

No	Initial reading	Final reading	Volume of KCNS (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

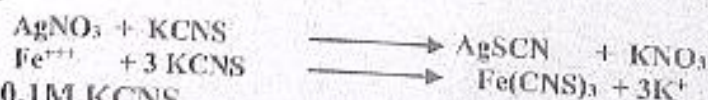
## EXPERIMENT

# 11

Determine the percentage of  $\text{Ag}^+$  ion in the given sample of  $\text{AgNO}_3$ , 12 g of which have been dissolved per  $\text{dm}^3$ . 0.1M KCNS solution is provided.

**Theory:** Silver ions can be determined by titrating the silver ion solution against standard KCNS solution by using ferric alum as an indicator which forms blood-red  $[\text{Fe}(\text{OH})_2(\text{SCN})]^{2+}$  at the end point. Sample solution is treated with  $\text{HNO}_3$  to make the medium acidic.

**Chemical Reactions:**



Standard solutions: 0.1M KCNS

Mole ratio:  $\text{AgNO}_3 : \text{KCNS} = 1 : 1$

Indicator: Ferric alum



**End point:** Permanent reddish tinge

**Procedure:**

1. 20 mL of the silver ion solution was taken in a flask and solution was acidified with 2 mL conc.  $\text{HNO}_3$  and flask was wrapped with black paper.
2. About 1 mL of 2% ferric alum solution was added to the titration flask as indicator. The contents were titrated against standard KCNS solution taken in the burette till the end point.
3. Initial and final burette readings were noted.
4. Volume of KCNS used was found by subtracting initial reading from final reading.
5. Titration was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Volume of $\text{Ag}^+$ ion solution taken	= 20.0 mL
Molarity of $\text{Ag}^+$ ion solution	= $M_1$ = ?
No. of mole of $\text{Ag}^+$ ion	= $n_1$ = 1
Molarity of KCNS solution	= $M_2$ = 0.1M
No. of mole of KCNS	= $n_2$ = 1
Volume of KCNS used	= $V_2$ = 20.0 mL

No	Initial reading	Final reading	Volume of KCNS (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{AgNO}_3) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{KCNS})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 20.0 \times 1}{1 \times 20} = 0.1 \text{ M}$$

Molarity of  $\text{Ag}^+$  ions =  $M_1 = 0.1 \text{ M}$

Amount of  $\text{Ag}^+$  ions per  $\text{dm}^3$  = Molarity of  $\text{Ag}^+$  ions  $\times$  Atomic mass of silver =  $0.1 \times 108 = 10.8 \text{ g per dm}^3$

Amount of  $\text{AgNO}_3$  per  $\text{dm}^3$  in the given sample = 12 g per  $\text{dm}^3$

$$\text{Percentage of } \text{Ag}^+ \text{ ions in the sample} = \frac{\text{Calculated amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{10.8}{12} \times 100$$

$$= 78.12 \%$$

Result: Percentage of  $\text{Ag}^+$  ions in the sample is 78.12%

**Exercise:** Determine the percentage of Ag in silver coin.

Hint: Dissolve the silver coin in small volume of  $\text{HNO}_3$  and make up the volume  $1 \text{ dm}^3$  by adding distilled water. Now titrate the solution as in experiment 11. Theory, chemical equation, procedure, and calculations are similar to experiment 11.

## EXPERIMENT



# 12

Determine the concentration of  $\text{Cl}^-$  in the given sample solution of NaCl by using fluorescein. 0.1M silver nitrate solution is provided.

**Theory:** This titration is an example of Fajan's method of chloride determination which makes use of adsorption indicators such as fluorescein and dichlorofluorescein. In this method, dichlorofluorescein is used as an indicator; the end-point is marked by the green suspension turning pink. Prior to the end-point of the titration, chloride ions remain in excess. They adsorb on the  $\text{AgCl}$  surface, imparting a negative charge to the particles. After the end-point, excess silver(I) ions adsorb on the  $\text{AgCl}$  surface, imparting a positive charge. Anionic dyes such as dichlorofluorescein are attracted to the particles, and undergo a colour change upon adsorption, representing the end-point.



**Chemical Reactions:**

**Mole Ratio:**  $\text{AgNO}_3 : \text{Cl}^- = 1:1$

**Standard solutions:** 0.1M  $\text{AgNO}_3$

**Indicator:** fluorescein

**End point:** Pinkish red ppt

**Procedure:**

1. 10 mL of the chloride ion solution was taken in a flask and 10 drops of indicator was added.
2. The contents were titrated against standard  $\text{AgNO}_3$  solution taken in the burette till the end point.
3. Initial and final burette readings were noted.
4. Volume of  $\text{AgNO}_3$  used was found by subtracting initial reading from final reading.
5. Titration was repeated thrice to get the concordant readings.

**OBSERVATIONS AND CALCULATIONS**

Volume of  $\text{Cl}^-$  ions solution taken = 10.0 mL

Molarity of  $\text{Cl}^-$  ions solution =  $M_1$  ?

No. of mole of  $\text{Cl}^-$  ions =  $n_1 = 1$

Molarity of  $\text{AgNO}_3$  solution =  $M_2 = 0.1\text{M}$

No. of mole of  $\text{AgNO}_3$  =  $n_2 = 1$

Volume of  $\text{AgNO}_3$  used =  $V_2 = 10.0\text{ mL}$

Substituting these values in molarity equation

$$(\text{Cl}^-) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 10.0} = 0.1\text{M}$$

Molarity of  $\text{Cl}^-$  ions =  $M_1 = 0.1\text{M}$

Amount of  $\text{Cl}^-$  ions per  $\text{dm}^3$  = Molarity of  $\text{Cl}^-$  ions  $\times$  Atomic mass of  $\text{Cl}^- = 0.1 \times 35.5 = 3.5\text{ g per dm}^3$

Amount of  $\text{Cl}^-$  per  $\text{dm}^3$  in the given sample = 3.5 g per  $\text{dm}^3$

**Result:** The given solution contains 3.5 g chloride ions per  $\text{dm}^3$

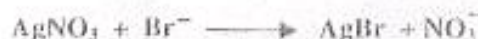
No	Initial reading	Final reading	Volume of KCNS (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

**EXPERIMENT****13**

Determine the concentration of  $\text{Br}^-$  in the given sample solution of  $\text{NaBr}$  by using fluorescein. 0.1M silver nitrate solution is provided.

**Theory:** This titration is an example of Fajan's method of halide determination which makes use of adsorption indicators such as fluorescein, eosine and dichlorofluorescein. In this method eosine is preferred over fluorescein and dichlorofluorescein; the end-point is marked by the appearance of sudden red coloured ppt. Prior to the end-point of the titration, bromide ions remain in excess. They adsorb on the  $\text{AgBr}$  surface, imparting a negative charge to the particles. Past the end-point, excess silver(I) ions adsorb on the  $\text{AgBr}$  surface, imparting a positive charge. Anionic dyes such as dichlorofluorescein are attracted to the particles, and undergo a colour change upon adsorption, representing the end-point.

**Chemical Reactions:**

**Mole Ratio:**  $\text{AgNO}_3 : \text{Br}^- = 1:1$

**Standard solutions:** 0.1M  $\text{AgNO}_3$

**Indicator:** Eosine



End point: Pinkish red ppt

### Procedure:

1. 10 ml. of the bromide solution was taken in a flask and 10 drops of indicator was added.
2. The contents were titrated against standard  $\text{AgNO}_3$  solution taken in the burette till the end point.
3. Initial and final burette readings were noted.
4. Volume of  $\text{AgNO}_3$  used was found by subtracting initial reading from final reading.
5. Titration was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Volume of  $\text{Br}^-$  ions solution taken = 10.0 mL.  
 Molarity of  $\text{Br}^-$  ions solution =  $M_1$  ?  
 No. of mole of  $\text{Br}^-$  ions =  $n_1 = 1$   
 Molarity of  $\text{AgNO}_3$  solution =  $M_2 = 0.1\text{M}$   
 No. of mole of  $\text{AgNO}_3$  =  $n_2 = 1$   
 Volume of  $\text{AgNO}_3$  used =  $V_2 = 10.0$  mL.

No	Initial reading	Final reading	Volume of KCNS (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{Br}^-) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{AgNO}_3)$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 10.0} = 0.1\text{M}$$

Molarity of  $\text{Br}^-$  ions =  $M_1 = 0.1\text{M}$

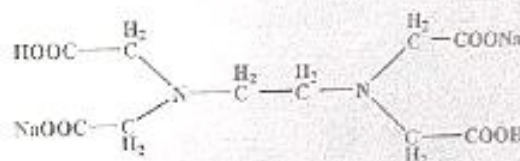
Amount of  $\text{Br}^-$  ions per  $\text{dm}^3$  = Molarity of  $\text{Br}^-$  ions  $\times$  Atomic mass of  $\text{Br}^- = 0.1 \times 80 = 8.0$  g per  $\text{dm}^3$

Amount of  $\text{Br}^-$  per  $\text{dm}^3$  in the given sample = 8.0 g per  $\text{dm}^3$

Result: The given solution contains 8.0 g bromide ions per  $\text{dm}^3$

## COMPLEXOMETRIC TITRATIONS

Complex formation of Ca, Mg, etc with  $\text{EDTA}^{4-}$  (Disodium dihydrogen ethylenediamine tetra acetate dihydrate,  $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ , 372.25) can be used for the titrimetric analysis of metal cations. The following conditions of the complex formation are important.



1. The complexes  $[\text{M}(\text{EDTA})]^{(n-4)+}$  are very stable; the equilibrium is  $\sim 100\%$  to the side of the complexes.
2. The complexes are labile; the equilibria are established instantaneously.  

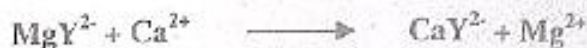
$$\text{M}^{n+} + \text{EDTA}^{4-} \rightleftharpoons [\text{M}(\text{EDTA})]^{(n-4)+}$$
3. The stoichiometry of the complexes is definite,  $\text{M}^{n+} / \text{EDTA}^{4-} = 1/1$ , because  $\text{EDTA}^{4-}$  occupies all the coordination sites of the metal.
4. There are indicators to detect the equivalence point. These are dyes which form a complex with the metal cation and are displaced by  $\text{edta}^{4-}$  at the equivalence point. The colour of the complex "M-indicator" differs from that of the free indicator (analogy to the acid/base indicators, where the colour change at the equivalence point is due to the deprotonation of the "H-indicator").
5. The  $\text{pK}_a$  of  $\text{H}_4\text{EDTA}$  are: 2.0; 2.7; 6.2 and 10.2. Therefore  $\text{H}_3\text{O}^+$  and  $\text{M}^{n+}$  compete to bind to  $\text{EDTA}^{4-}$  and the stability of  $[\text{M}(\text{EDTA})]^{(n-4)+}$  complexes is strongly pH-dependent. As a consequence, complexometric titrations have to be performed in buffered solutions.

EDTA is represented by the symbol  $\text{H}_4\text{Y}$ , which recognizes the fact that it is a tetraprotic acid. The four hydrogens in the formula refer to the four acidic hydrogens on the four carboxyl groups. It is the unprotonated ligand  $\text{Y}^{4-}$  that is responsible for the formation of complexes with metal ions. The titration is performed by adding a standard solution of EDTA to the sample containing the Ca. The reaction that takes place is the following:

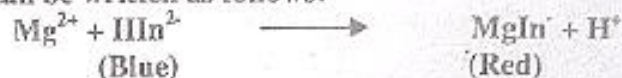




Before the equivalence point, the  $\text{Ca}^{2+}$  concentration is nearly equal to the amount of unchelated (unreacted) calcium since the dissociation of the chelate is slight. At the equivalence point and beyond, Ca is determined from the dissociation of the chelate at the given pH. The equivalence point is detected through the use of an indicator which is itself a chelating agent. The specific indicator used is Eriochrome Black T. It contains three ionisable protons and we will represent it by the formula  $\text{H}_3\text{In}$ . In neutral or somewhat basic solutions, it is a doubly dissociated ion,  $\text{HIn}^{2-}$ , which is blue in colour. Eriochrome Black T cannot be used as an indicator for the titration of calcium with EDTA, since it forms too weak a complex with calcium to give a sharp end point. Therefore, a solution containing the magnesium complex of EDTA,  $\text{MgY}^{2-}$ , is introduced into the titration mixture. Since  $\text{Ca}^{2+}$  forms a more stable complex with EDTA than magnesium, the following reaction occurs:



The magnesium that is released in this manner then reacts with the doubly ionized ion of the Eriochrome Black T. The complex that is formed between magnesium and that ion is red, hence at the start of the Ca titration the solution is red. This reaction can be written as follows:



The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining calcium ion that has not been complexed. After all the calcium has reacted the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $\text{MgIn}^{2-}$ ), to give  $\text{MgY}^{2-}$  and  $\text{HIn}^{2-}$  and thereby giving a blue colour at the end point.



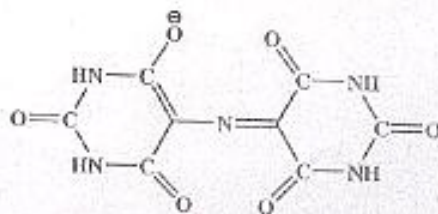
The titration is conducted at a buffered solution at about pH 10.

## Preparation of Reagents

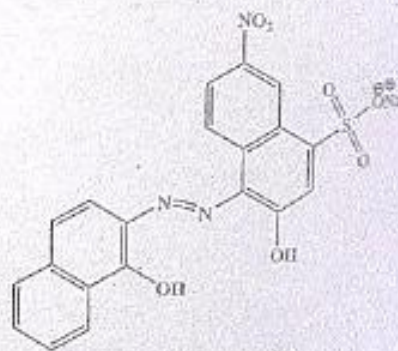
1. **0.10M standard solution of EDTA:** Dry about 10 g of EDTA dihydrate,  $\text{Na}_2\text{H}_2\text{Y}_2 \cdot 2\text{H}_2\text{O}$ , in a drying oven at  $80^\circ\text{C}$  for one hour. Then accurately weigh out about 9.30 g. Quantitatively transfer the EDTA into a 250 mL volumetric flask, add distilled water with mixing then dilute to the mark with distilled water. Mix well by inverting and shaking the tightly stoppered flask. Primary standards of EDTA cannot be prepared. EDTA solutions should be standardized against  $\text{ZnSO}_4$  or  $\text{MgSO}_4$  of very high purity. Water used in EDTA solution preparations should be free from polyvalent metal ions and preferably distilled through all Pyrex glass. Label this solution "Standard EDTA".

### 2. Indicator solutions:

- a. **Eriochrome Black-T:** It is sodium -(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate and also known as Solochrome Black-T. It is used in EDTA titrations at pH 6.5 or more. It produces sharp colour change from blue to red when metal ions such as Mg, Zn, Cd, Cu, Al, Fe etc are added to its solution at pH 7-11. Solution is prepared by dissolving 0.2 g dye in 15 mL of triethanolamine and 5 mL absolute ethanol.



Murexide



Eriochrome Black-T

- b. **Murexide:** It is ammonium salt of purpuric acid. It is used in direct titration of EDTA with Ca at pH 11. The colour change is from blue to violet. The solution is prepared by dissolving 0.5 g of the compound in sufficient amount of water and filtering the solution.
3. **Buffer solution of pH 10:** Dissolve 17.5 g ammonium chloride in 100 mL water in 250 mL measuring flask and add 142 mL conc. Ammonia solution.
4. **10% KOH:** Dissolve 10 g KOH in 100 mL water.



# EXPERIMENT



1

Determine the amount of  $Mg^{2+}$  in sample solution using Eriochrome Black-T. 0.1M EDTA solution is provided.

**Theory:**  $Mg^{2+}$  ions in sample solution are estimated by complexometric titration. Complex formation between  $Mg$  ions and EDTA is quantitative and can be monitored by using Eriochrome Black-T as indicator. Indicator ions react with  $Mg^{2+}$  ions to form wine red colour complex in the beginning.



The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $Mg^{2+}$  ion that has not been complexed. After all the  $Mg^{2+}$  has reacted, the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $MgIn^{+}$ ), to give  $MgY^{2-}$  and  $HIn^{2-}$  and thereby giving a blue colour at the end point.



**Standard Solution:** 0.1M EDTA

**Mole ratio:** EDTA:  $Mg^{2+}$  1:1

**Indicator:** Eriochrome Black-T

**End point:** Blue colour

**Procedure:**

- 20 mL  $Mg^{2+}$  ions solution was taken in the titration flask and 2 mL buffer of pH 10 was added to it.
- 2-3 drops of indicator were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
- Initial and final burette readings were noted.
- Volume of EDTA used was found by subtracting initial reading from final reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of  $Mg^{2+}$  ions solution taken =  $V_1$  = 20.0 mL

Molarity of  $Mg^{2+}$  ions solution =  $M_1$  = ?

No. of mole of  $Mg^{2+}$  ions =  $n_1$  = 1

Molarity of EDTA solution =  $M_2$  = 0.1M

No. of mole of EDTA =  $n_2$  = 1

Volume of EDTA used =  $V_2$  = 10.0 mL

Substituting these values in molarity equation

$$(Mg^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \text{ (EDTA)}$$

$$M_1 = \frac{n_2 V_1}{n_1 V_2} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05M$$

Molarity of  $Mg^{2+}$  ions =  $M_1$  = 0.05M

Amount of  $Mg^{2+}$  per  $dm^3$  = Molarity of  $Mg^{2+}$  ions  $\times$  Atomic mass of  $Mg^{2+}$  =  $0.05 \times 24.3 = 1.215g \text{ per } dm^3$

Amount of  $Mg^{2+}$  per  $dm^3$  in the given sample = 1.215g per  $dm^3$

**Result:** The given solution contains 1.215g  $Mg^{2+}$  ions per  $dm^3$

No	Initial Burette reading	Final Burette reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

## Alternative Method of Calculations

1 mL of 0.1M EDTA = 2.432mg of  $Mg^{2+}$  ions

10 mL of 0.1M EDTA =  $10 \times 2.432 \text{ mg of } Mg^{2+} \text{ ions} = 24.32 \text{ mg of } Mg^{2+} \text{ ions}$

20 mL of sample contains  $Mg^{2+}$  = 24.32 mg of  $Mg^{2+}$  ions

1000  $cm^3$  of sample contains  $Mg^{2+}$  =  $\frac{24.32}{20} \times 1000 = 1216 \text{ mg per } dm^3 = 1.216 \text{ g per } dm^3$



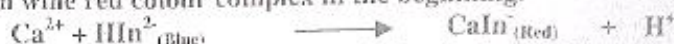
## EXPERIMENT



# 2

Determine the amount of  $\text{Ca}^{2+}$  per  $\text{dm}^3$  in sample solution using Eriochrome Black-T. 0.1M EDTA solution is provided.

**Theory:**  $\text{Ca}^{2+}$  ions in sample solution are estimated by complexometric titration. Complex formation between Ca ions and EDTA is quantitative and can be monitored by using Eriochrome Black-T or Murexide as indicator. Indicator ions react with  $\text{Ca}^{2+}$  ions to form wine red colour complex in the beginning.



The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $\text{Mg}^{2+}$  ion that has not been complexed. After all the  $\text{Mg}^{2+}$  has reacted, the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $\text{MgIn}^{-}$ ), to give  $\text{MgY}^{2-}$  and  $\text{HIn}^{2-}$  and thereby giving a blue colour at the end point.



**Standard Solution:** 0.1M EDTA

**Mole ratio:** EDTA:  $\text{Ca}^{2+}$  = 1:1

**Indicator:** Eriochrome Black-T

**End point:** Blue colour

**Procedure:**

1. 20 mL  $\text{Ca}^{2+}$  ions solution was taken in the titration flask and 2 mL buffer of pH 10 was added to it.
2. 2-3 drops of indicator were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
3. Initial and final burette readings were noted.
4. Volume of EDTA used was found by subtracting initial reading from final reading.
5. Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of  $\text{Ca}^{2+}$  ions solution taken =  $V_1$  = 20.0 mL

Molarity of  $\text{Ca}^{2+}$  ions solution =  $M_1$  = ?

No. of mole of  $\text{Ca}^{2+}$  ions =  $n_1$  = 1

Molarity of EDTA solution =  $M_2$  = 0.1M

No. of mole of EDTA =  $n_2$  = 1

Volume of EDTA used =  $V_2$  = 10.0 mL

Substituting these values in molarity equation

$$(\text{Ca}^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{EDTA})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05\text{M}$$

Molarity of  $\text{Ca}^{2+}$  ions =  $M_1$  = 0.05M

Amount of  $\text{Ca}^{2+}$  per  $\text{dm}^3$  = Molarity of  $\text{Ca}^{2+}$  ions  $\times$  Atomic mass of  $\text{Ca}^{2+}$  =  $0.05 \times 40 = 2.0$  g per  $\text{dm}^3$

Amount of  $\text{Ca}^{2+}$  per  $\text{dm}^3$  in the given sample = 2.0 g per  $\text{dm}^3$

**Result:** The given solution contains 2.0 g  $\text{Ca}^{2+}$  ions per  $\text{dm}^3$

No	Initial reading	Final reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

### Alternative Method of Calculations

1 mL of 0.1M EDTA = 4.008 mg of  $\text{Mg}^{2+}$  ions

10 mL of 0.1M EDTA =  $10 \times 4.008$  mg of  $\text{Mg}^{2+}$  ions = 40.08 mg of  $\text{Mg}^{2+}$  ions

20 mL of sample contains  $\text{Mg}^{2+}$  = 40.08 mg of  $\text{Mg}^{2+}$  ions

1000  $\text{cm}^3$  of sample contains  $\text{Mg}^{2+}$  =  $\frac{40.08}{20} \times 1000 = 2004$  mg per = 2.0 g per  $\text{dm}^3$



# EXPERIMENT



# 3

Determine the amount of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  per  $\text{dm}^3$  in Hard water using 0.1M EDTA solution is provided

**Theory:** Hardness of water is due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions which can be estimated by complexometric titration. Complex formation between Ca & Mg ions and EDTA is quantitative and can be monitored by using Eriochrome Black-T and Murexide as indicator. Titration involving Eriochrome Black-T gives total amount of Ca & Mg ions. Titration with standard EDTA solution using murexide indicator gives only amount of  $\text{Ca}^{2+}$  ions.  $\text{Mg}^{2+}$  ions can be found by subtracting  $\text{Ca}^{2+}$  ions from total of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. Indicator ions react with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to form wine red colour complex in the beginning.



The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions that has not been complexed. After all the  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  has reacted, the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $\text{MgIn}$ ), to give  $\text{MgY}^{2-}$  and  $\text{HIn}^{2-}$  and thereby giving a blue colour at the end point.



Where M = Ca or Mg

## A. Estimation of Total $\text{Ca}^{2+}$

Standard Solution: 0.1M EDTA

Mole ratio: EDTA:  $\text{Ca}^{2+}$  = 1:1

Indicator: Murexide

End point: Blue colour

Procedure:

- 20 mL sample of hard water was taken in the titration flask and 5 mL of 10% KOH solution was added to it.
- 10 drops of murexide were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
- Initial and final burette readings were noted.
- Volume of EDTA used was found by subtracting initial reading from final reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of hard water taken	= $V_1$	= 20.0 mL
Molarity of hard water	= $M_1$	= ?
No. of mole of $\text{Ca}^{2+}$ ions	= $n_1$	= 1
Molarity of EDTA solution	= $M_2$	= 0.1M
No. of mole of EDTA	= $n_2$	= 1
Volume of EDTA used	= $V_2$	= 10.0 mL

Substituting these values in molarity equation

$$\begin{aligned} (\text{Ca}^{2+}) \frac{M_1 V_1}{n_1} &= \frac{M_2 V_2}{n_2} (\text{EDTA}) \\ M_1 &= \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} \\ &= 0.05\text{M} \end{aligned}$$

No	Initial Burette reading	Final Burette reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

Molarity of  $\text{Ca}^{2+}$  ions =  $M_1$  = 0.05M  
 Amount of  $\text{Ca}^{2+}$  per  $\text{dm}^3$  = Molarity of  $\text{Ca}^{2+}$  ions x Atomic mass of  $\text{Ca}^{2+}$  =  $0.05 \times 40 = 2.0 \text{ g per dm}^3$



Amount of  $\text{Ca}^{2+}$  per  $\text{dm}^3$  in the given sample = 2.0 g per  $\text{dm}^3$

### B. Estimation of $\text{Mg}^{2+}$

Standard Solution: 0.1M EDTA

Mole ratio: EDTA:  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  = 1:1

Indicator: Eriochrome Black-T

End point: Blue colour

Procedure:

- 20 mL of hard water was taken in the titration flask and 2 mL buffer of pH 10 was added to it.
- 2-3 drops of indicator were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
- Initial and final burette readings were noted.
- Volume of EDTA used was found by subtracting initial reading from final reading.
- Experiment was repeated thrice to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

Volume of hard water taken =  $V_1$  = 20.0 mL

Molarity of hard water =  $M_1$  = ?

No. of mole of  $\text{Ca}^{2+}$  ions =  $n_1$  = 1

Molarity of EDTA solution =  $M_2$  = 0.1M

No. of mole of EDTA =  $n_2$  = 1

Volume of EDTA used =  $V$  = 20.0 mL

Actual volume of EDTA used for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  = 20.0 mL

Volume of EDTA used for  $\text{Ca}^{2+}$  only = 10.0 mL

Volume of EDTA used for  $\text{Mg}^{2+}$  only  $V_2$  = 20.0 mL - 10.0 mL = 10.0 mL

Substituting these values in molarity equation

$$(\text{Mg}^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{EDTA})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05\text{M}$$

Molarity of water sample with respect to  $\text{Mg}^{2+}$  = 0.05M

Amount of  $\text{Mg}^{2+}$  per  $\text{dm}^3$  = Molarity of  $\text{Mg}^{2+}$  ions  $\times$  Atomic mass of  $\text{Mg}^{2+}$  =  $0.05 \times 24 = 1.2$  g per  $\text{dm}^3$

Amount of  $\text{Mg}^{2+}$  per  $\text{dm}^3$  in the given sample of hard water = 1.2 g per  $\text{dm}^3$

Result: The given sample of hard water contains 2.0 g  $\text{Ca}^{2+}$  ions and 1.2 g  $\text{Mg}^{2+}$  ions per  $\text{dm}^3$ .

## EXPERIMENT



# 4

Determine the percentage of  $\text{Ca}^{2+}$  ion in lime stone .0.1M EDTA solution is provided

Theory: Lime stone is mainly  $\text{CaCO}_3$ . Lime stone is treated with HCl and solution is neutralized with KOH.  $\text{Ca}^{2+}$  ions can be titrated against standard solution of EDTA using murexide indicator. Complex formation between  $\text{Ca}^{2+}$  ions and EDTA is quantitative,



The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $\text{Mg}^{2+}$  ion that has not been complexed. After all the  $\text{Mg}^{2+}$  has reacted, the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes



favourably with the red magnesium-indicator complex ( $\text{MgIn}^+$ ), to give  $\text{MgY}^{2-}$  and  $\text{HIn}^+$  and thereby giving a blue colour at the end point.



Standard Solution: 0.1M EDTA

Mole ratio: EDTA:  $\text{Ca}^{2+}$  = 1:1

Indicator: Murexide

End point: Blue colour

Procedure:

1. 2 g lime stone was dissolved in minimum amount of HCl and solution was diluted to 250 mL.
2. 20 mL of  $\text{Ca}^{2+}$  solution was taken in the titration flask and 10 mL of 10% KOH solution was added to it.
3. 10 drops of murexide were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
4. Initial and final burette readings were noted.
5. Volume of EDTA used was found by subtracting initial reading from final reading.
6. Experiment was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Volume of  $\text{Ca}^{2+}$  ions solution taken =  $V_1$  = 20.0 mL  
 Molarity of  $\text{Ca}^{2+}$  ions solution =  $M_1$  = ?  
 No. of mole of  $\text{Ca}^{2+}$  ions =  $n_1$  = 1  
 Molarity of EDTA solution =  $M_2$  = 0.1M  
 No. of mole of EDTA =  $n_2$  = 1  
 Volume of EDTA used =  $V_2$  = 10.0 mL

No	Initial Burette reading	Final Burette reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{Ca}^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \text{ (EDTA)}$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05\text{M}$$

Molarity of  $\text{Ca}^{2+}$  ions =  $M_1$  = 0.05M

Amount of  $\text{Ca}^{2+}$  per  $\text{dm}^3$  = Molarity of  $\text{Ca}^{2+}$  ions  $\times$  Atomic mass of  $\text{Ca}^{2+}$  =  $0.05 \times 40 = 2.0 \text{ g per dm}^3$

Amount of lime stone in 250 mL solution = 2.0 g

Amount of lime stone in 1  $\text{dm}^3$  solution =  $\frac{2}{250} \times 1000 = 8.0 \text{ g}$

Percentage purity =  $\frac{\text{Calculated amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{2}{8} \times 100 = 25\%$

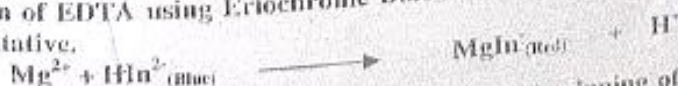
Result: The given solution contains 25%  $\text{Ca}^{2+}$  ions per  $\text{dm}^3$

### EXPERIMENT



Determine the percentage of  $\text{Mg}^{2+}$  ion in the sample of magnesite. 0.1M EDTA solution is provided

Theory: Magnesium is in the form of  $\text{MgCO}_3$  in magnesite. It is treated with HCl and  $\text{Mg}^{2+}$  ions are titrated against standard solution of EDTA using Eriochrome Black-T as indicator. Complex formation between  $\text{Mg}^{2+}$  ions and EDTA is quantitative.



The solution is titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $\text{Mg}^{2+}$  ions that has not been complexed. After all the  $\text{Mg}^{2+}$  has reacted, the next portion of



EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $MgIn$ ), to give  $MgY^{2-}$  and  $HIn^{2-}$  and thereby giving a blue colour at the end point.



Standard Solution: 0.1M EDTA

Mole ratio: EDTA:  $Ca^{2+}$  1:1

Indicator: Eriochrome Black-T

End point: Blue colour

Procedure:

1. 5 g magnesite was dissolved in minimum amount of HCl and solution neutralized with KOH solution. Water was added to this solution to make the volume 250 mL.
2. 20 mL of  $Mg^{2+}$  ions solution was taken in the titration flask and diluted to 100 mL. 2 mL buffer of pH 10 was added to it.
3. 2-3 drops of indicator were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
4. Initial and final burette readings were noted.
5. Volume of EDTA used was found by subtracting initial reading from final reading.
6. Experiment was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Volume of  $Mg^{2+}$  ions solution taken =  $V_1$  = 20.0 mL  
 Molarity of  $Mg^{2+}$  ions solution =  $M_1$  = ?  
 No. of mole of  $Mg^{2+}$  ions =  $n_1$  = 1  
 Molarity of EDTA solution =  $M_2$  = 0.1M  
 No. of mole of EDTA =  $n_2$  = 1  
 Volume of EDTA used =  $V_2$  = 10.0 mL

Substituting these values in molarity equation

$$(Mg^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} \text{ (EDTA)}$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05M$$

Molarity of  $Mg^{2+}$  ions =  $M_1$  = 0.05M

Amount of  $Mg^{2+}$  per  $dm^3$  = Molarity of  $Mg^{2+}$  ions  $\times$  Atomic mass of  $Mg^{2+}$  =  $0.05 \times 24.3 = 1.215$  g per  $dm^3$

Amount of magnesite in 250 mL solution = 5.0 g

Amount of magnesite in 1  $dm^3$  solution =  $\frac{5}{250} \times 1000 = 20.0$  g

Percentage purity =  $\frac{\text{Calculated amount per } dm^3}{\text{Given amount per } dm^3} \times 100 = \frac{1.215}{20} \times 100 = 6.075\%$

Result: The given sample contains 6.075%  $Ca^{2+}$  ions per  $dm^3$

No	Initial Burette reading	Final Burette reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

Dip

### EXPERIMENT



6

Determine the percentage of  $Mn^{2+}$  ion in the sample. 0.1M EDTA solution is provided.

Theory:  $Mn^{2+}$  ions can be titrated against standard solution of EDTA using Eriochrome Black-T as indicator. Complex formation between  $Mn^{2+}$  ions and EDTA is quantitative.





The solution is titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $\text{Mn}^{2+}$  ions that has not been complexed. After all the  $\text{Mn}^{2+}$  has reacted, the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $\text{MnIn}$ ), to give  $\text{MnY}^{2-}$  and  $\text{HIn}^{2-}$  and thereby giving a blue colour at the end point.



Standard Solution: 0.1M EDTA

Mole ratio: EDTA:  $\text{Mn}^{2+}$  = 1:1

Indicator: Eriochrome Black-T

End point: Blue colour

Procedure:

1. 20 mL of  $\text{Mn}^{2+}$  ions solution was taken in the titration flask and diluted to 100 mL. 0.1 g hydroxylammoniumchloride and 3 mL triethanol amine was added. 5 mL buffer of pH 10 was added to it adjust the pH 10.
2. 2-3 drops of indicator were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
3. Initial and final burette readings were noted.
4. Volume of EDTA used was found by subtracting initial reading from final reading.
5. Experiment was repeated thrice to get the concordant readings.

Hydroxylammoniumchloride is added to manganese solution to prevent oxidation of manganese. Triethanol amine prevents the precipitation of  $\text{Mn}(\text{OH})_2$ .

### OBSERVATIONS AND CALCULATIONS

Volume of $\text{Mn}^{2+}$ ions solution taken	= $V_1$ = 20.0 mL
Molarity of $\text{Mn}^{2+}$ ions solution	= $M_1$ = ?
No. of mole of $\text{Mn}^{2+}$ ions	= $n_1$ = 1
Molarity of EDTA solution	= $M_2$ = 0.1M
No. of mole of EDTA	= $n_2$ = 1
Volume of EDTA used	= $V_2$ = 10.0 mL

No	Initial Burette reading	Final Burette reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

Substituting these values in molarity equation

$$(\text{Mn}^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{EDTA})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05\text{M}$$

$$\text{Molarity of } \text{Mn}^{2+} \text{ ions} = M_1 = 0.05\text{M}$$

$$\text{Amount of } \text{Mn}^{2+} \text{ per dm}^3 = \text{Molarity of } \text{Mn}^{2+} \text{ ions} \times \text{Atomic mass of } \text{Mn}^{2+} = 0.05 \times 55 = 2.75 \text{ g per dm}^3$$

Result: The given sample contains 2.75 g manganese per  $\text{dm}^3$

## EXPERIMENT



# 7

Determine the percentage of  $\text{Ca}^{2+}$  in the given sample solution using Eriochrome Black-T and NaCl as indicator. 0.1M EDTA standard solution is provided.

Theory:  $\text{Ca}^{2+}$  ions in sample solution are estimated by complexometric titration. Complex formation between  $\text{Ca}$  ions and EDTA is quantitative and can be monitored by using Eriochrome Black-T or Murexide as indicator. Indicator ions react with  $\text{Ca}^{2+}$  ions to form wine red colour complex in the beginning.





The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining  $Mg^{2+}$  ion that has not been complexed. After all the  $Mg^{2+}$  has reacted, the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favourably with the red magnesium-indicator complex ( $MgIn$ ), to give  $MgY^{2-}$  and  $HIn^{2-}$  and thereby giving a blue colour at the end point.



**Standard Solution:** 0.1M EDTA

**Mole ratio:** EDTA:  $Ca^{2+}$  = 1:1

**Indicator:** Eriochrome Black-T

**End point:** Blue colour

Solution of Eriochrome Black-T is unstable. Therefore solid Eriochrome Black-T is unstable is mixed with very small amount of NaCl, KCl or  $Na_2SO_4$  and reagent is powdered. NaCl stabilizes the indicator. Behaviour of indicator towards EDTA remains unaffected

**Procedure:**

1. 20 mL  $Ca^{2+}$  ions solution was taken in the titration flask and 2 mL buffer of pH 10 was added to it.
2. 2-3 drops of indicator were added and the solution was titrated against standard EDTA solution taken in the burette until pure blue colour appeared.
3. Initial and final burette readings were noted.
4. Volume of EDTA used was found by subtracting initial reading from final reading.
5. Experiment was repeated thrice to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Volume of  $Ca^{2+}$  ions solution taken =  $V_1$  = 20.0 mL.  
 Molarity of  $Ca^{2+}$  ions solution =  $M_1$  = ?  
 No. of mole of  $Ca^{2+}$  ions =  $n_1$  = 1  
 Molarity of EDTA solution =  $M_2$  = 0.1M  
 No. of mole of EDTA =  $n_2$  = 1  
 Volume of EDTA used =  $V_2$  = 10.0 mL  
 Substituting these values in molarity equation

No	Initial Burette reading	Final Burette reading	Volume of EDTA mL
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.1

Volume used = 10.0 mL

$$(Ca^{2+}) \frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2} (\text{EDTA})$$

$$M_1 = \frac{M_2 V_2 n_1}{n_2 V_1} = \frac{0.1 \times 10.0 \times 1}{1 \times 20.0} = 0.05M$$

Molarity of  $Ca^{2+}$  ions =  $M_1$  = 0.05M

Amount of  $Ca^{2+}$  per  $dm^3$  = Molarity of  $Ca^{2+}$  ions  $\times$  Atomic mass of  $Ca^{2+}$  =  $0.05 \times 40 = 2.0$  g per  $dm^3$

Amount of  $Ca^{2+}$  per  $dm^3$  in the given sample = 2.0 g per  $dm^3$

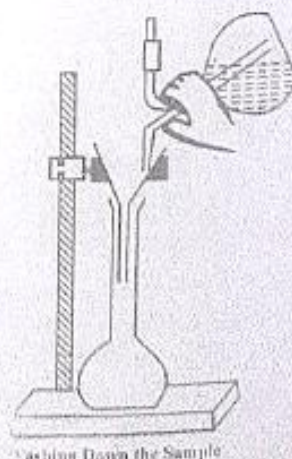
**Result:** The given solution contains 2.0 g  $Ca^{2+}$  ions per  $dm^3$

## GRAVIMETRIC ANALYSIS

### Introduction:

Gravimetric analysis is the type of analysis in which constituent to be "determined" is precipitated from a solution in the form of a stable, insoluble compound of accurately known composition, which is filtered off, washed free from adhering solution, dried, ignited and weighed. The weight of the particular constituent present in the original solution is then calculated from the weight and composition of the precipitate.

### Gravimetric operations





Gravimetric analysis consists of the following operations:

- A. Preparation of solution of a definite quantity of the substance under consideration in a suitable solvent.
  - B. Precipitation in the form of a compound of known composition
  - C. Filtering and washing the precipitate
  - D. Drying
  - E. Igniting
  - F. Weighing the precipitate to constant weight.
- A. *Preparation of solution:* A suitable weight of the substance to be analyzed is very accurately weighed on a watch glass. The weighed sample is quantitatively transferred in a previously cleaned beaker. Wash down the particles sticking to the watch glass by means of a spray of water from the wash bottle as shown in the Figure.
- B. *Precipitation:* Precipitation is method to separate out the constituent under determination as an insoluble compound of known composition. Precipitate is obtained by adding an appropriate reagent (precipitant) in slight excess to a dilute and hot solution of the weighed sample with constant stirring of the solution. The precipitate is then digested, i.e., warmed and allowed to stand with the hot mother liquor for some time. Allow the precipitate to settle down and add a drop or two of the same precipitant to the upper clear layer as shown in the figure. If turbidity is produced, more of the precipitant is added. If no turbidity appears, precipitant is not added.
- C. *Filtering and washing the precipitate:* A quantitative filter paper is used for the purpose. For coarse precipitate use Whatman No. 41 and for fine precipitate use No. 42 or blue band filter paper and note the weight of the ash of the filter paper selected. To remove the more firmly sticking particles on the interior of the beaker and on the stirring rod, moisten them with water and rub gently with the help of a rubber-tipped glass rod (often called policeman). Wash the policeman before removing it from the beaker. Transfer the loosened particles into the filter as before. Wash the precipitate several times with a suitable wash liquid. Since the precipitate is formed in the presence of one or more soluble compounds, the later be removed completely by washing by distilled water or preferably by some suitable wash-liquid, the wash-liquid chosen should be such that it has the least solvent effect on the precipitate and does not peptize it when the electrolytes have been washed out.
- D. *Drying:* When the precipitate has been washed completely allow the last washing to drain completely and then remove any liquid from the funnel stem with a filter paper cutting. Cover the funnel by crumpling a piece of paper over it rim. Make some holes in the cover with a pencil. These holes will allow the steam to escape during heating but will prevent dust particles from dropping into the filter paper cone. Rest the funnel in one of the holes of the plate of the air-oven as shown in the figure.
- E. *Ignition:* When the ppt. is completely dried, take out the funnel from the air oven. Take off the filter paper cone from the funnel, and keep it over a sheet of glazed paper (black for white ppt. or white for coloured ppt.) the cone pointing upwards. Loosen the precipitate by pressing it from sides gently between the finger, and thus bulk of the ppt. falls down on the glazed paper. Bring together the particles of the ppt. with the help of a camel hair brush and cover the ppt. With an inverted. Take another sheet of glazed paper and keep it on the table. A clay pipe triangle is made into a tripod stand thus prepared is kept on the glazed sheet. The previously weighed crucible with lid is taken and the crucible is kept on the clay pipe triangle tripod stand. The filter paper cone with any ppt. adhering is then folded and held with a clean pair of tongs over the weighed crucible. The tip of the folded filter paper is kept just over the crucible. The paper is then burnt slowly with the projected flame of the burner.
- F. *Heating to constant weight:* The crucible is then kept over on a clay pipe triangle over a tripod stand. Any ash fallen on the glazed sheet is transferred very carefully into the crucible with the help of the camel hair brush and then start heating. The lid of the crucible should be either kept slightly displaced or it should be momentarily lifted up with the help tongs after the intervals of every 5-10 minutes. The carbonized paper (black) should be completely converted into ash (grey). Cool the crucible and keep it again on the clay pipe triangle tripod stand which has been kept over the glazed sheet of paper. The



main bulk of the ppt. kept on the small glazed sheet of paper is then transferred quantitatively into the crucible with the help of the camel hair brush. Any precipitate falling on the large sheet of paper is also transferred to the crucible. Now keep the crucible again on the tripod stand and heat it after any necessary treatment. Cool the crucible with the lid in desiccators and weigh it. Repeat the process of heating, cooling and weighing, till the final weight is constant.

### Filtration through sintered glass crucibles:

Sintered glass crucibles are made of resistance glass for example, pyrex or jena and have a porous disc of sintered, ground glass fused into the body of the crucible. The fused in fritted filter disc can be obtained in various degrees of porosity. Sintered glass crucible is usually supported in a special holder known as adapter, by means of a wide rubber tube, the bottom of the crucible should be quite free from the funnel and from the rubber gasket, in order to be quite sure that the filtrate does not come into contact with the rubber. The adapter passes through a one holed rubber bung into a large filter flask of about 750 mL capacity. The filtration is performed under reduced pressure, when vacuum is produced in the filter flask, atmospheric pressure forces the liquid through the pores in the glass filter while the precipitate is retained. These crucibles can be safely heated to 200 °C.

## EXPERIMENT



1

Determine the weight of  $\text{Ba}^{2+}$  in one  $\text{dm}^3$  of the given solution gravimetrically.

### Principle:

$\text{Ba}^{2+}$  ions can be precipitated as  $\text{BaCrO}_4$  by the reaction of  $\text{Ba}^{2+}$  ions with  $\text{K}_2\text{CrO}_4$  or  $(\text{NH}_4)_2\text{CrO}_4$  solution.

### Chemical Reaction:



### Procedure:

- 20.0 mL of the given  $\text{Ba}^{2+}$  ion solution was diluted up to 100 mL with distilled water.
- 10 mL of N- acetic acid and 5g ammonium chloride was added to the above solution and heated to boiling point.
- 10%  $\text{K}_2\text{CrO}_4$  solution was added drop wise to hot solution of  $\text{Ba}^{2+}$  ions with constant stirring till complete precipitation. The solution was boiled gently for 2-3 minutes. The supernatant liquid was checked to ensure complete precipitation.
- Precipitate was filtered with a pre-weighed sintered glass crucible and dried in oven at 118°C for 30 minutes.
- The precipitate was cooled in desiccator and weighed.

## OBSERVATIONS AND CALCULATIONS

Mass of crucible	=	20.0 g	
Mass of crucible + ppt.	=	20.5 g	
Mass of $\text{BaCrO}_4$ ppt.	=	20.50 - 20.0	= 0.50 g
$\text{BaCrO}_4$	=	$\text{Ba}^{2+}$	
Molecular mass of $\text{BaCrO}_4$	=	253.83 g/mol.	
Atomic mass of $\text{Ba}^{2+}$	=	137.33 g/mol	
So 253.33 g $\text{BaCrO}_4$	=	137.33 g $\text{Ba}^{2+}$	
0.50 g $\text{BaCrO}_4$	=	$\frac{137.33 \times 0.50}{253.33}$	= 0.271 g



20.0 mL of the given solution contains  $\text{Ba}^{2+}$

1 dm<sup>3</sup> of the given solution contains  $\text{Ba}^{2+}$

$$= \frac{0.271 \text{ g}}{0.27 \times 1000} = 13.5 \text{ g}$$

Result: The given solution contains 1.355 g/dm<sup>3</sup> of  $\text{Ba}^{2+}$

Exercise:

1. Determine the percentage of  $\text{Ba}^{2+}$  in the given solution

Hints: Follow the same procedure as in experiment No.1 and calculate the percentage of  $\text{Ba}^{2+}$  as under:

1 dm<sup>3</sup> solution contains  $\text{Ba}^{2+}$  ions = 1.355 g

100 mL solution contains  $\text{Ba}^{2+}$  ions =  $1.355 \text{ g}/1000 \times 100 = 0.14\%$

2. The given solution of  $\text{BaCl}_2$  contains 15 g impure sample dissolved per dm<sup>3</sup>. Calculate the percentage purity of the given sample.

Hints: Follow the same procedure as in experiment No.1 and calculate the percentage purity of  $\text{BaCl}_2$

## EXPERIMENT



# 2

Determine the weight of  $\text{Pb}^{2+}$  in one dm<sup>3</sup> of the given solution gravimetrically

Principle:

$\text{Pb}^{2+}$  ions can be precipitated as  $\text{PbCrO}_4$  by the reaction of  $\text{Pb}^{2+}$  ions with  $\text{K}_2\text{CrO}_4$  or  $(\text{NH}_4)_2\text{CrO}_4$  solution in acidic solution.

Chemical Reaction:



Procedure:

1. 20.0 mL of the given  $\text{Pb}^{2+}$  ion solution was diluted up to 100 mL with distilled water.
2. 10 mL of N-acetic was added to the above solution and heated to boiling point.
3. 10%  $\text{K}_2\text{CrO}_4$  solution was added drop wise to hot solution of  $\text{Pb}^{2+}$  ions with constant stirring till complete precipitation. The solution was boiled gently for 2-3 minutes. The supernatant liquid was checked to ensure complete precipitation.
4. Precipitate was filtered with a pre-weighed sintered glass crucible and dried in oven at 118°C for 30 minutes.
5. The precipitate was cooled in desiccator and weighed.

## OBSERVATIONS AND CALCULATIONS

Mass of crucible	=	20.0 g	
Mass of crucible + ppt.	=	20.5 g	
Mass of $\text{PbCrO}_4$ ppt.	=	20.50 - 20.0	= 0.50 g
$\text{PbCrO}_4$	=	$\text{Pb}^{2+}$	*
Molecular mass of $\text{PbCrO}_4$	=	323.0 g/mol	
Atomic mass of $\text{Pb}^{2+}$	=	137.33 g/mol	
So			
323.0 g $\text{PbCrO}_4$	=	207 g $\text{Pb}^{2+}$	

$$\begin{aligned} 0.50 \text{ g } \text{PbCrO}_4 &= \frac{207.0 \times 0.50}{323.0} = 0.32 \text{ g} \\ 20.0 \text{ mL of the given solution contains } \text{Pb}^{2+} &= \frac{0.32 \text{ g}}{0.32 \times 1000} = 16.0 \text{ g} \\ 1 \text{ dm}^3 \text{ of the given solution contains } \text{Pb}^{2+} &= \frac{16.0 \text{ g}}{20} = 16.0 \text{ g} \end{aligned}$$

Result: The given solution contains 16 g/dm<sup>3</sup> of  $\text{Pb}^{2+}$



**Exercise:**

- Find out the percentage purity of  $\text{Pb}(\text{CH}_3\text{COO})_2$  gravimetrically.
- Find out the amount of  $\text{Pb}(\text{NO}_3)_2$  in the 250 mL of the given solution gravimetrically.

**Hints:** Precipitate the  $\text{Pb}^{2+}$  ions as in experiment and calculate the percentage purity of  $\text{Pb}(\text{CH}_3\text{COO})_2$  and amount of  $\text{Pb}(\text{NO}_3)_2$  in 250 mL.

### Questions for viva voce examination

- Q 1 What is gravimetric analysis?  
 Ans. It is quantitative technique in which an insoluble compound is formed from the solution by some precipitating reagent and analyzed by weight
- Q 2 Name two precipitating reagents for  $\text{Ba}^{2+}$  ions?  
 Ans. Ammonium chromate and potassium chromate.
- Q 3 What is the function of acetic acid and ammonium chloride in the precipitation of  $\text{Ba}^{2+}$  by potassium chromate? Ans. It acts as buffer.
- Q 4 Define "Digestion" of precipitate?  
 Ans. Digestion is a phenomenon in which precipitate is allowed to remain in contact with hot liquor for few minutes on a water bath.
- Q 5 Why  $\text{BaCrO}_4$  is precipitated in neutral medium?  
 Ans.  $\text{BaCrO}_4$  is soluble in acidic medium therefore it is precipitated in neutral medium.
- Q 6 Why is precipitate digested?  
 Ans. Precipitate is digested to avoid co-precipitation and makes it coarse so that it can be filtered easily.
- Q 7 Why precipitate is cooled in desiccator?  
 Ans. Precipitate is cooled in desiccator to avoid absorption of moisture.
- Q 8 What is a desiccator? Ans. It is an apparatus used to remove moisture from a substance.
- Q 9 Name a desiccating agent? Ans. Calcium chloride.
- Q 10 How many filters can be used for filtration?  
 Ans. Ash less Filter Paper ii) Gouch crucibles iii) Sintered glass crucible
- Q 11 Define desiccating agent?  
 Ans. A substance which absorbs moisture is called desiccant or desiccating agent.
- Q 12 Give an example of desiccant?  
 Ans.  $\text{CaCl}_2$ ,  $\text{P}_2\text{O}_5$ , Silica gel or conc.  $\text{H}_2\text{SO}_4$
- Q 13 Why hot crucible is not weighed?  
 Ans. Air current produced inside the balance due to difference of temperature cause serious errors in weighing. Therefore hot objects are not weighed.

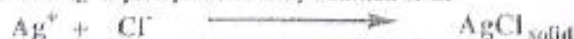
## Gravimetric analysis

Gravimetric analysis, by definition, includes all methods of analysis in which the final stage of the analysis involves weighing. The quantitative determination of a substance by precipitation followed by isolation and weighing of the precipitate is called gravimetric analysis.

The basic method of gravimetric analysis is fairly straightforward. A weighed sample is dissolved after which an excess of a precipitating agent is added. The precipitate which forms is filtered, dried or ignited and weighed. From the mass and known composition of the precipitate, the amount of the original ion can be determined.

For successful determinations the following criteria must be met;

- The desired substance must be completely precipitated. In most determinations the precipitate is of such low solubility that losses from dissolution are negligible. An additional factor is the "common ion" effect, this further reduces the solubility of the precipitate. When  $\text{Ag}^+$  is precipitated out by addition of  $\text{Cl}^-$



The (low) solubility of  $\text{AgCl}$  is reduced still further by the excess of  $\text{Cl}^-$  which is added, pushing the equilibrium to the right.

- The weighed form of the product should be of known composition.
- The product should be "pure" and easily filtered. It is usually difficult to obtain a product which is "pure", i.e. one which is free from impurities but careful precipitation and sufficient washing helps reduce the level of impurity.
- Weigh your product at room temperature. Never weigh hot substance. The process of heating, cooling and weighing should be repeated until a constant mass is obtained.



# Inorganic Preparations

## EXPERIMENT

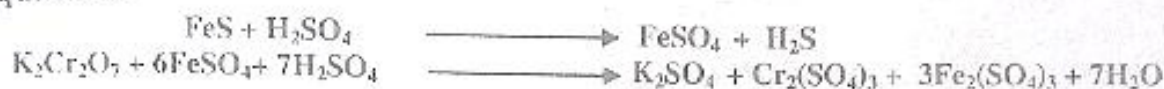


# 1

## Preparation of $\text{FeSO}_4$ from Kipp's Apparatus waste and determination of Fe in the sample

**Theory:** Kipp's waste is mainly  $\text{FeS}$  which can be converted into  $\text{FeSO}_4$  by reacting it with  $\text{H}_2\text{SO}_4$ . Fe is estimated in  $\text{FeSO}_4$  by titrating it with standard solution of  $\text{K}_2\text{Cr}_2\text{O}_7$ .

**Chemical Equations:**



### A. Preparation of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ from Kipp's Apparatus waste:

#### Procedure

- 100 mL of Kipp's waste was taken in china dish.
- Some iron filling and 20 mL dil.  $\text{H}_2\text{SO}_4$  was added to the Kipp's waste and contents were boiled.
- More iron fillings were added with constant stirring and boiling until evolution of hydrogen gas ceased to evolve.
- Solution was filtered while hot, filtrate was collected in a beaker and beaker was placed in cold water.
- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  crystallized out as light green crystals. Mother liquor was decanted and crystals were dried first in the folds of filter papers and then in air.

### B. Determination of percentage purity of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Mole ratio:  $\text{K}_2\text{Cr}_2\text{O}_7 : 6 \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 1:6$

Standard solution: 0.01M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution.

Indicator: Sodium diphenylamine sulphonate

End point: Violet blue colour.

#### Procedure:

- 2 g dried crystals of prepared  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  were dissolved in few mL of distilled water and volume was made 100 mL by adding distilled water.
- 10 mL of this  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution, 10 mL of dil.  $\text{H}_2\text{SO}_4$  and 10 mL of phosphoric acid were taken in the conical flask. 2-3 drops of indicator solution were added.
- Standard potassium dichromate solution was run from burette until the appearance of violet blue colour.
- Titration was repeated three or four times to get the concordant readings.

## OBSERVATIONS AND CALCULATIONS

No	Initial reading	Final reading	Volume (mL)
1	0.0	10.0	10.0
2	10.0	20.1	10.1
3	20.1	30.1	10.0

Volume used = 10 mL

Molarity of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution =  $M_1 = 0.01 \text{ M}$

Volume of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution =  $V_1 = 10.0 \text{ mL}$

No. of moles of  $\text{K}_2\text{Cr}_2\text{O}_7$  =  $n_1 = 1$

Molarity of  $\text{FeSO}_4$  solution =  $M_2 = ? \text{ M}$

Volume of  $\text{FeSO}_4$  solution =  $V_2 = 10.0 \text{ mL}$

No. of moles of  $\text{FeSO}_4$  =  $n_2 = 6$

Substituting the values in molarity equation



$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$M_2 = \frac{M_1 V_1 n_2}{n_1 V_2} = \frac{0.01 \times 10.0 \times 6}{1 \times 10} = 0.06 \text{ M}$$

Hence, the molarity of the  $\text{FeSO}_4$  solution = 0.06 M

Amount of  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  per  $\text{dm}^3$  = Molarity  $\times$  Molar mass of  $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$  =  $0.06 \times 278 = 16.68 \text{ g}$

Amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 100 mL = 2 g

Amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  per  $\text{dm}^3$  =  $2/100 \times 1000 = 20 \text{ g}$

Percentage purity of ferrous sulphate =  $\frac{\text{Calculated amount per dm}^3}{\text{Given amount per dm}^3} \times 100$

$$= \frac{16.68}{20.0} \times 100 = 83.4\%$$

**Result:** Hence the purity of the sample is 83.4%

## EXPERIMENT



# 2

### Preparation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ from Copper turnings and determination of purity of the prepared sample

**Theory and Chemical Reactions:** Conc.  $\text{H}_2\text{SO}_4$  reacts with metallic copper to form  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Percentage of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in the sample can be estimated by titrating the sample solution against standard solution of sodium tetrathionate.



#### A. Preparation of copper sulphate

##### Procedure:

- 15 mL conc.  $\text{H}_2\text{SO}_4$  was added to 5 g copper turnings taken in a beaker. The contents were warmed gently until copper turnings dissolved.
- Mixture was allowed to cool. Solid mass was separated by decantation and dissolved in about 50 mL water and filtered.
- Filtrate was concentrated by evaporating the water and allowed to cool while  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was crystallized.
- Crystals were obtained by decanting the mother liquor and dried in folds of filter paper and air.

#### B. Determination of percentage purity of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Mole ratio:  $\text{CuSO}_4 : \text{Na}_2\text{S}_2\text{O}_3 = 1:2$

Standard solution: 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$

Indicator: Starch solution

End point: Light blue colour

##### Procedure:

- 2 g  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  sample was dissolved in 100 mL distilled water.
- 5 mL of this solution was taken in the iodine flask and about 1-2 g KI was added.
- Standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution was run from burette until the solution acquired lemon yellow colour. 1-2 mL starch solution was added at this point which imparted blue colour to the solution.  $\text{Na}_2\text{S}_2\text{O}_3$  solution was added further from burette until blue colour just disappeared. Initial and final burette readings were noted.



4. Titration was repeated three or four times to get the concordant readings.

### OBSERVATIONS AND CALCULATIONS

Molarity of  $\text{CuSO}_4$  solution =  $M_1 = ?$  M  
 Volume of  $\text{CuSO}_4$  solution =  $V_1 = 5.0$  mL  
 No. of moles of  $\text{CuSO}_4$  =  $n_1 = 1$   
 Molarity of  $\text{Na}_2\text{S}_2\text{O}_3$  solution =  $M_2 = 0.05$  M  
 Volume of  $\text{Na}_2\text{S}_2\text{O}_3$  solution used =  $V_2 = 15.0$  mL  
 No. of moles of  $\text{Na}_2\text{S}_2\text{O}_3$  =  $n_2 = 2$   
 Substituting the values in molarity equation

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 5.0}{1} = \frac{0.05 \times 15.0 \times 1}{2}$$

$$M_1 = 0.075 \text{ M}$$

Hence, the molarity of the given solution  
 Amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per  $\text{dm}^3$

$$= 0.075 \text{ M}$$

$$= \text{Molarity} \times \text{Molar mass of } \text{Na}_2\text{S}_2\text{O}_3$$

$$= 0.075 \times 249.6 = 18.72 \text{ g per dm}^3$$

$$= 2 \text{ g}$$

$$= 2/100 \times 1000 = 20.0 \text{ g}$$

Amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dissolved in 100 mL  
 Amount of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  per  $\text{dm}^3$

$$\text{Percentage purity of copper sulphate} = \frac{\text{Calculated amount per dm}^3}{\text{Given amount per dm}^3} \times 100 = \frac{18.72}{20.0} \times 100$$

$$= 93.6\%$$

Result: Hence the percentage purity of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is 93.6%

## EXPERIMENT



# 3

### Preparation of Ferric alum.

**Theory:** Ferric alum is double salt of iron and ammonium. It is prepared from ferrous sulphate which is oxidized to ferric sulphate first by  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . Both solutions of ferric sulphate and ammonium sulphate are then mixed and crystallized.



#### Procedure:

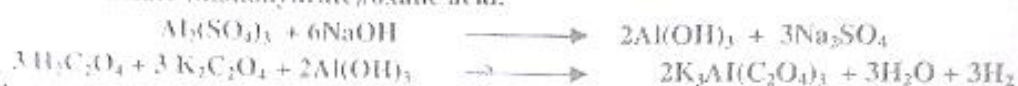
- 0.05 Mole (13.9 g) ferrous sulphate was dissolved in 25 mL of boiling water and 3 mL dil.  $\text{H}_2\text{SO}_4$  was added to acidify solution. The solution was boiled and 10 mL conc.  $\text{HNO}_3$  was added to the reaction mixture to oxidize the ferrous to ferric.
- Solution was boiled until brown fumes ceased to evolve to remove nitric oxide.
- 0.05 Mole (6.6 g) of ammonium sulphate was dissolved in small amount of water in a separate beaker.
- Two solutions were mixed and heated to point of crystallization.
- Solution was cooled and crystals of ferric alum were separated by decantation and dried in folds of filter paper and air.

Yield: 20g (72.4 %).



**EXPERIMENT****4****Preparation of potassium trioxalatealuminate**

**Theory:** Potassium trioxalatealuminate is prepared by the reaction of freshly prepared aluminum hydroxide and potassium oxalate (monohydrate)/oxalic acid.

**Procedure:**

1.  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 6.66 g (0.01 mole) was dissolved in 100 mL water and NaOH solution was added to this solution with constant stirring. The ppt. was filtered and washed with water.
2.  $\text{K}_2\text{C}_2\text{O}_4$ , 5g and  $\text{H}_2\text{C}_2\text{O}_4$ , 5g was dissolved in 100 mL. Freshly prepared  $\text{Al}(\text{OH})_3$  was added to this solution and mixture was boiled for 5 minutes, cooled and filtered.
3. Filtrate was concentrated by evaporation and potassium trioxalatealuminate was crystallized.
4. Crystals were separated by decantation and dried.
5. Yield was calculated from mass of the dry crystals.

Yield: 6.6g (80%)

**EXPERIMENT****5****Preparation of Hypo.**

**Theory:** Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) is prepared by refluxing the aqueous solution of sodium sulphate and sulphur.

**Procedure:**

1. 5.68g  $\text{Na}_2\text{SO}_4$  (0.04 mole) and 2 g sulphur was taken in 100 mL round bottom flask and 50 mL water was added to the mixture. A reflux condenser was fitted in the flask and mixture was refluxed for about 1 hour (till the reaction mixture was no more alkaline).
2. Condenser was removed and excess sulphur was filtered off.
3. The filtrate was concentrated by evaporation till crystallization.
4. Crystals were separated by decantation and dried.
5. Yield was calculated from mass of the dry crystals.

Yield: 7.7g (83%)



## EXPERIMENT

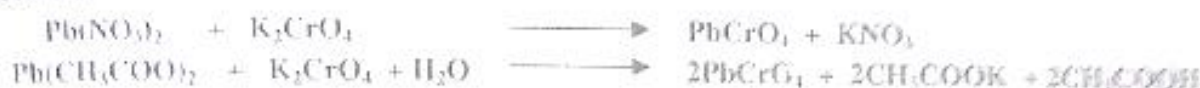


6

### Preparation of lead chromate (Chrome yellow)

**Theory:** Chrome yellow is obtained as yellow ppt by double displacement reaction between lead nitrate and potassium chromate. Lead chromate can also be prepared by reaction of lead acetate and potassium dichromate.

**Chemical reactions:**



**Procedure:**

1. 5.1 g lead nitrate was dissolved in 50 mL distilled water and solution was made clear by adding acetic acid.
2. Similarly 3.0 g potassium chromate was dissolved in 50 mL distilled water
3. Potassium chromate solution was added slowly to solution of lead nitrate with constant stirring.
4. Mixture was allowed to stand while ppt. of lead chromate settled.
5. Ppt. was filtered and washed three times with water and dried.
6. Yield was calculated.

### OBSERVATIONS AND CALCULATIONS

Mass of dried ppt.	=	4.0 g			
Mass of lead nitrate taken	=	5.1 g	=	$5.1/331$	= 0.015 mol
Mass of potassium chromate	=	3.0 g	=	$3/194$	= 0.015 mol
Hence No. of moles of $\text{PbCrO}_4$ formed			=	0.015 mol	
Mass of lead chromate to be formed	=	$0.015 \times \text{Molecular mass of } \text{PbCrO}_4$	=	$0.015 \times 323.19$	= 4.84 g
Percentage Yield	=	$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$	=	$\frac{4.0}{4.84} \times 100$	= 82.6 %

## EXPERIMENT



7

### Preparation of microcosmic salt.

**Theory:** Sodium ammonium hydrogen phosphate ( $\text{Na}(\text{NH}_4)\text{HPO}_4$ ) is commonly known as microcosmic salt. It is prepared by mixing equimolar quantities of disodium hydrogen phosphate and ammonium chloride.

**Chemical reaction:**



**Procedure:**

1. 0.1 mole (5.35 g) ammonium chloride and 0.1 mole (14.1 g)  $\text{Na}_2\text{HPO}_4$  were dissolved in minimum amount of boiling water.
2. Hot mixture was allowed to cool and crystals separated after some time.
3. Crystals were obtained by decanting the mother liquor and dried in the folds of filter paper and oven at  $120^\circ\text{C}$ .
4. Yield was calculated.



## OBSERVATIONS AND CALCULATIONS

Mass of dried ppt.	=	12.0 g		
Mass of ammonium chloride taken	=	5.35 g	=	5.35/53.5 = 0.1 mol
Mass of $\text{Na}_2\text{HPO}_4$	=	14.1 g	=	14.1/141 = 0.1 mol
Hence No. of moles of $\text{Na}(\text{NH}_4)\text{HPO}_4$ formed	=	0.1 mol		
Mass of $\text{Na}(\text{NH}_4)\text{HPO}_4$ to be formed	=	$0.1 \times \text{Molecular mass of } \text{Na}(\text{NH}_4)\text{HPO}_4 = 0.1 \times 137 = 13.7 \text{ g}$		
Percentage Yield	=	$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 = \frac{12.0}{13.7} \times 100 = 87.5 \%$		

## EXPERIMENT



8

## Preparation of ammonium copper(II)sulphate.

**Theory:** Ammonium copper(II)sulphate can be prepared by mixing equimolar quantities of copper sulphate pentahydrate and ammonium sulphate.

**Chemical reaction:**



**Procedure:**

1. 0.01 mole (2.49 g)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 0.01 mole (1.32 g)  $(\text{NH}_4)_2\text{SO}_4$  were dissolved in minimum amount of boiling water and filtered hot.
2. The filtrate was evaporated to crystallization point and allowed to cool and crystals were obtained by decanting the mother liquor and dried in the folds of filter paper and oven at  $120^\circ\text{C}$ .
3. Yield was recorded.

## OBSERVATIONS AND CALCULATIONS

Mass of dried ppt.	=	2.5 g		
Mass of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ taken	=	2.49 g	=	2.49/249 = 0.01 mol
Mass of $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ to be formed	=	$0.01 \times \text{Molecular mass of } \text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ $= 0.01 \times 381.8 = 3.8 \text{ g}$		
Percentage Yield	=	$\frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100 = \frac{2.5}{3.8} \times 100 = 65.7 \%$		

## PAPER CHROMATOGRAPHY

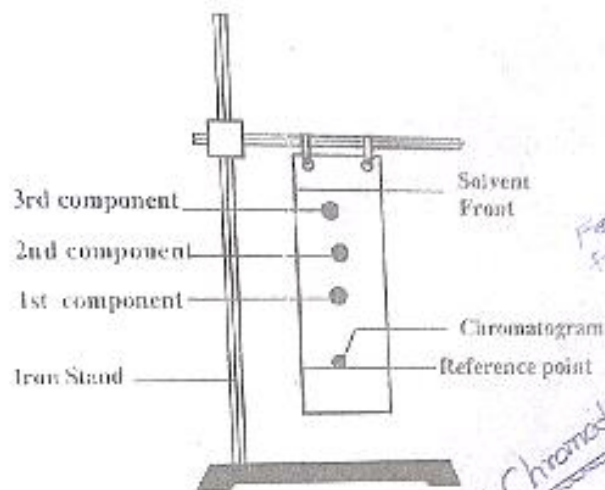
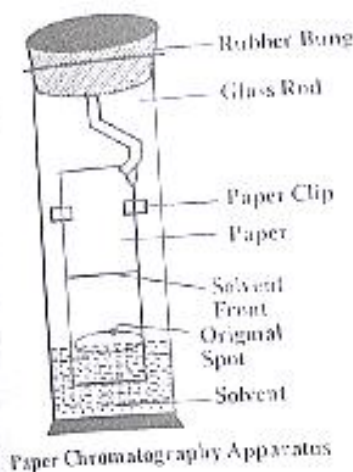
## Introduction

Chromatography is a separation technique based on distribution of components of the mixture between the mobile and the stationary phases. Separation of components occurs due to different solubilities of the components in the mobile and stationary phases. Water molecules held by paper act as stationary phase and solvent acts as a mobile phase. Paper is used as a support for stationary phase in paper chromatography which is based on partition of solute between mobile and stationary phase.



$R_f$  Value:  $R_f$  is the abbreviation of retardation factor and mathematically it is calculated as given below:

$$R_f = \frac{\text{Distance travelled by the solute in cm}}{\text{Distance travelled by the solvent front in cm}}$$



*Paper Chromatography*

## EXPERIMENT



# 1

Separate  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  in the given mixture by paper chromatography.

**Principle:** Paper chromatography is a separation technique in which separation of components occurs due to different solubilities of the components in the mobile and stationary phases. Water molecules held by paper act as stationary phase and solvent acts as a mobile phase. Paper is used as a support for stationary phase in paper chromatography.

$R_f$  value (retardation factor) determines the extent or efficiency of separation. Mathematically,  $R_f$  is calculated as:

$$R_f = \frac{\text{Distance travelled by the solute in cm}}{\text{Distance travelled by the solvent front in cm}}$$

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook,

**Chemicals:** Solvent, (Acetone, Conc. HCl and water), 1% solution of rubeanic acid in ethanol,  $\text{NH}_4\text{OH}$ , so Solutions of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ . (Dissolve  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ ,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in water and 2M HCl so as to give 10  $\mu\text{g}$  of each ion per 0.01 mL of solution.) ions. 0.1% ethanolic solution of rubeanic acid as spraying agent

### Procedure:

1. Developing solvent was prepared by mixing 22 mL, acetone, 2 mL conc. HCl and 1 mL water in the cylinder and it was closed and kept undisturbed for 30 minutes.
2. A 12 cm long and 5 cm wide whatman No. 1 filter paper was taken and base line was drawn with lead pencil at a distance of 1.5 cm from the bottom.
3. Three crosses labelled as A, B, C, D, E and M were marked at equal distances with lead pencil.
4. The drops of the  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  ions solutions were placed on marks A, B, C, D, E, respectively.
5. A drop of mixture solution of these ions was placed on mark M with a jet. Filter paper strip was dried and suspended in the cylinder containing solvent mixture.
6. Strip was removed when solvent reached at the upper end, dried and held on beaker containing liquid ammonia till smell of HCl disappeared.



- Dried strip was sprayed with 0.1% sodium pentacyanoamineferrate(II)/Rubeanic acid/ diphenyl carbazide solutions.
- Solvent front and centres of the ions were marked and distances measured.
- $R_f$  of the standard ions and ions from the mixture was calculated.

### OBSERVATIONS AND CALCULATIONS

Distance travelled by solvent = X cm

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed with rubeanic acid	$R_f$ of ions from the mixture
1	A ( $\text{Cu}^{2+}$ )				Green	
2	B ( $\text{Mn}^{2+}$ )				*Pale pink	
3	C ( $\text{Ni}^{2+}$ )				Blue	
4	D ( $\text{Co}^{2+}$ )				Orange	
5	E ( $\text{Zn}^{2+}$ )				**Red	

\* Colour with diphenyl carbazide, \*\* Colour with sodium pentacyanoamineferrate(II)/Rubeanic acid

### EXPERIMENT



Separate and identify basic radicals of Group I in the given mixture by paper chromatography.

**Principle:** Same as in Experiment 1.

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook.

**Chemicals:** Solvent, (Acetone, Conc. HCl and water), 5% solution of  $\text{K}_2\text{CrO}_4$  in water,  $\text{NH}_4\text{OH}$ , Solutions of  $\text{Pb}^{2+}$ ,  $\text{Ag}^+$ , and  $\text{Hg}_2^{2+}$  (Dissolve nitrates of these ions separately in 2M  $\text{HNO}_3$  so as to give 10 $\mu\text{g}$  of each ion per 0.01 mL of solution) ions.

**Locating Agent:** 5% aqueous solution of  $\text{K}_2\text{CrO}_4$

**Procedure:** Same as in Experiment 1.

### OBSERVATIONS AND CALCULATIONS

Distance travelled by solvent = X cm

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed with $\text{K}_2\text{CrO}_4$	$R_f$ of ions from the mixture
1	A ( $\text{Pb}^{2+}$ )				Yellow	
2	B ( $\text{Ag}^+$ )				Red	
3	C ( $\text{Hg}_2^{2+}$ )				Brown	



**EXPERIMENT****3**

Separate and identify basic radicals of Group IIA in the given mixture by paper chromatography.

**Principle:** Same as in Experiment 1.

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook.

**Chemicals:** Solvent, (Ethanol = 8.8 mL, 5M HCl)  $\text{NH}_4\text{OH}$ , so Solutions of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Hg}^{2+}$ . Dissolve Nitrates of these ions separately in conc.  $\text{HNO}_3$  so as to give  $10\mu\text{g}$  of each ion per 0.01 mL of solution. Ions.

**Locating Agent:** 0.05% dithizone solution in  $\text{CCl}_4$

**Procedure:** Same as in Experiment 1.

**OBSERVATIONS AND CALCULATIONS**

Distance travelled by solvent = X cm

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed with 0.05% dithizone	$R_f$ of ions from the mixture
1	A ( $\text{Pb}^{2+}$ )				Red	
2	B ( $\text{Bi}^{3+}$ )				Brown	
3	C ( $\text{Cu}^{2+}$ )				Blue	
4	D ( $\text{Cd}^{2+}$ )				Pink	
5	E ( $\text{Hg}^{2+}$ )				Red	

**EXPERIMENT****4**

Separate and identify basic radicals of Group IIB in the given mixture by paper chromatography.

**Principle:** Same as in Experiment 1.

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook.

**Chemicals:** Solvent, ( $\text{C}_2\text{H}_5\text{COOCH}_3 = 7.5\text{ mL}$ , Acetone = 2.5 mL, conc.  $\text{HCl} = 0.05\text{ mL}$ )  $\text{NH}_4\text{OH}$ , so Solutions of  $\text{As}^{3+}$  as arsenite,  $\text{Sb}^{3+}$  as  $\text{SbCl}_3$  and  $\text{Sn}^{4+}$  as  $\text{SnCl}_4$ . (Dissolve these salts separately in water so as to give  $10\mu\text{g}$  of each ion per 0.01 mL of solution)

**Locating Agent:** Saturated solution of  $\text{H}_2\text{S}$  in water

**Procedure:** Same as in Experiment 1.

**OBSERVATIONS AND CALCULATIONS**

Distance travelled by solvent = X cm



No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	R <sub>f</sub> of Standard ions	Colours of ions, sprayed with H <sub>2</sub> S water	R <sub>f</sub> of ions from the mixture
1	A (As <sup>3+</sup> )				Light yellow	
2	B (Sb <sup>3+</sup> )				Orange	
3	C (Sn <sup>4+</sup> )				Dark brown	

## EXPERIMENT



# 5

Separate and identify basic radicals of Group III in the given mixture by paper chromatography.

**Principle:** Same as in Experiment 1.

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook,

**Chemicals:** Solvent, ( Acetone = 8.6 mL, conc. HCl = 0.6 mL, water = 0.8 mL ) NH<sub>4</sub>OH, Solutions of Al<sup>3+</sup> as AlCl<sub>3</sub>, Cr<sup>3+</sup> as CrCl<sub>3</sub> and Fe<sup>3+</sup> as FeCl<sub>3</sub>. Dissolve these salts separately in water so as to give 10μg of each ion per 0.01 mL of solution.)

**Locating Agent:** 0.2 % Aluminone solution in water, 0.5% Alizarin in ethanol

**Procedure:** Same as in Experiment 1. Prepare two strips. Spray one strip with 0.2 % Aluminone and second with 0.5% Alizarin

## OBSERVATIONS AND CALCULATIONS

Distance travelled by solvent = X cm

Result with 0.2 % Aluminone

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	R <sub>f</sub> of Standard ions	Colours of ions, sprayed with 0.2 % Aluminone	R <sub>f</sub> of ions from the mixture
1	A ( Al <sup>3+</sup> )				Red	
2	B ( Fe <sup>3+</sup> )				Purple	
3	C ( Cr <sup>3+</sup> )				Dark brown	

Result with 0.5 % Alizarin

2	C ( Cr <sup>3+</sup> )				Orange red	
3	B ( Fe <sup>3+</sup> )				Purple	



# EXPERIMENT



6

Separate and identify basic radicals of Group IV in the given mixture by paper chromatography.

Principle: Same as in Experiment 1.

Apparatus: Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook.

Chemicals: Solvent. (Acetone = 8.0 mL, Conc HCl = 0.6 mL and water = 0.8 mL), 1% solution of rubeanic acid in ethanol,  $\text{NH}_4\text{OH}$ , so Solutions of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  (Dissolve  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ ,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{CoCl}_2$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in water and 2M HCl so as to give  $10\mu\text{g}$  of each ion per 0.01 mL of solution.)

Locating agent: (i) 0.1% ethanolic solution of rubeanic acid (ii) 5% Aq. Sodium diethyldithiocarbamate (iii) 0.05% ethanolic solution of Zircon

Procedure: Same as in Experiment 1. Develop three chromatograms of same size under identical conditions. Spray three strips with different locating agent.

## OBSERVATIONS AND CALCULATIONS

Distance travelled by solvent = X cm

Result with rubeanic acid solutions

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed with rubeanic acid	$R_f$ of ions from the mixture
1	A ( $\text{Ni}^{2+}$ )				Blue	
2	B ( $\text{Co}^{2+}$ )				Olive green	

Result with 5% Aq. Sodium diethyldithiocarbamate solutions

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed with *SDEDTC	$R_f$ of ions from the mixture
3	A ( $\text{Ni}^{2+}$ )				Pale green	
4	C ( $\text{Mn}^{2+}$ )				Purple	
5	B ( $\text{Co}^{2+}$ )				Green	

\* SDEDTC = Sodium diethyldithiocarbamate

Result with 0.05% ethanolic solution of Zircon

No	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed with *SDEDTC	$R_f$ of ions from the mixture
3	A ( $\text{Ni}^{2+}$ )				Green	
4	C ( $\text{Mn}^{2+}$ )				Pale green	
5	D ( $\text{Zn}^{2+}$ )				Blue	



**EXPERIMENT****7**

Separate and identify basic radicals of Group V in the given mixture by paper chromatography.

**Principle:** Same as in Experiment 1.

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook,

**Chemicals:** Solvent, (Methanol = 8.2 mL, conc. HCl = 0.9 mL, water = 0.9 mL)  $\text{NH}_4\text{OH}$ , Solutions of  $\text{Ba}^{2+}$  as  $\text{BaCl}_2$ ,  $\text{Sr}^{2+}$  as  $\text{SrCl}_2$  and  $\text{Ca}^{2+}$  as  $\text{CaCl}_2$ . (Dissolve these salts separately in water so as to give  $10\mu\text{g}$  of each ion per 0.01 mL of solution.)

**Locating Agent:** (i) 2 % Sodium rhodizonate in water  
(ii) 2.5 % Pyrogallol in 0.5M  $\text{NH}_4\text{OH}$

**OBSERVATIONS AND CALCULATIONS**

**Procedure:** Same as in Experiment 1. Develop two chromatograms. Spray one strip with 2 % Sodium rhodizonate solution and second with 2.5 % Pyrogallol

Distance travelled by solvent = X cm

**Result with 2 % Sodium rhodizonate**

No	Ions	Distance travelled by standard ions	Distance travelled by ions from mixture	$R_f$ of Standard ions	Colours of ions, sprayed 2 % Sodium rhodizonate	$R_f$ of ions from the mixture
1	A ( $\text{Ba}^{2+}$ )				Red	
2	B ( $\text{Sr}^{2+}$ )				Pink	

**Result with 2.5% Pyrogallol**

1	C ( $\text{Ca}^{2+}$ )				Violet brown	
2	A ( $\text{Ba}^{2+}$ )				Violet brown	
3	B ( $\text{Sr}^{2+}$ )				Violet brown	

**EXPERIMENT****8**

Separate and identify radicals of Group VI given in the mixture by paper chromatography

**Principle:** Same as in Experiment 1.

**Apparatus:** Whatman Filter paper No.1, Cylinder or Jar or Chromatographic Tank, Capillary Tube Jet, Rubber Bung with hook,

**Chemicals:** Solvent, (Methanol = 5.6 mL, Isopropanol = 3.4 mL, water = 1.0 mL)  $\text{NH}_4\text{OH}$ , Solutions of  $\text{Mg}^{2+}$  as  $\text{MgCl}_2$ ,  $\text{Na}^+$  as  $\text{NaCl}$ ,  $\text{NH}_4^+$  as  $\text{NH}_4\text{Cl}$  and  $\text{K}^+$  as  $\text{KCl}$ . Dissolve these salts separately in water so as to give  $10\mu\text{g}$  of each ion per 0.01 mL of solution.)

**Locating Agent:** (i) 10 % Cobaltinitrite containing 2 drops of 0.5 % silvernitrate in water  
(ii) 0.02 % Magnesone in 0.2M  $\text{NaOH}$



## OBSERVATIONS AND CALCULATIONS

**Procedure:** Same as in Experiment 1. Develop two chromatograms. Spray one strip with 10 % cobaltinitrite solution and second with 0.02 % magneson.

Distance travelled by solvent = X cm

**Result with 10 % Cobaltinitrite containing 2 drops of 0.5% silver nitrate**

N <sup>o</sup>	Ions	Distance travelled by standard ions from base line in cm	Distance travelled by ions from mixture	R <sub>f</sub> of Standard ions	Colours of ions, sprayed 10 % cobaltinitrite	R <sub>f</sub> of ions from the mixture
1	A (K <sup>+</sup> )				Yellow	
2	B (NH <sub>4</sub> <sup>+</sup> )					
3	C (Na <sup>+</sup> )					

**Result with 2.5% Pyrogallol**

4	D (Mg <sup>2+</sup> )				Blue	
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## QUESTIONS FOR VIVA-VOCE

Q. 1 Define Chromatography?

Ans. It is a broad range of physical methods used to separate and to analyze complex mixtures. The components to be separated are distributed between two phases: a *stationary phase* and a *mobile phase* which percolates through the stationary bed.

Q. 2 What is stationary phase in paper chromatography?

Ans. Water absorbed in paper acts as a stationary phase in the paper chromatography.

Q. 3 What is the function of paper in this technique?

Ans. Paper acts as a support for stationary phase in paper chromatography.

Q. 4 Name some techniques of chromatography?

- (i) Gas Chromatography (GC) (ii) Column Chromatography  
(iii) Gas Liquid Chromatography (GLC) (iv) Thin Layer Chromatography (TLC)

Q. 5 What are applications of paper chromatography?

Ans. It is used for separation of cations, anions, pigments, inks and complex mixture of amino acids etc.

Q. 6 What is the principle of paper chromatography?

Ans. Paper chromatography is based upon the different rates of flow of different components of mixture with mobile phase.

Q. 7 What is significance of R<sub>f</sub> Value?

Ans. R<sub>f</sub> value indicates the relative rates of flow of the components of the mixture. A component with higher R<sub>f</sub> value move faster than that with less R<sub>f</sub> value.

Q. 8 How will you calculate R<sub>f</sub> Value.

$$R_f = \frac{\text{Distance travelled by the solute in cm}}{\text{Distance travelled by the solvent front in cm}}$$

Q. 9 Name stationary phase in paper chromatography?

Ans. Water absorbed on paper surface acts as a stationary phase in paper chromatography.

Q. 10 What is the criterion of choice of solvent?

Ans. Solvent should not react with the substance to be separated.

Q. 11 Name the locating agent for Cd<sup>2+</sup>, and Pb<sup>2+</sup>.

Ans. Alcoholic solution of rubenic acid.

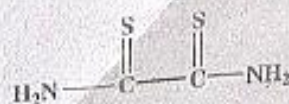
Q. 12 Give the composition of solvent for the separation of Ni<sup>2+</sup>, Co<sup>3+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>.

Ans. Acetone = 2 parts

Ter. Butyl alcohol = 2 parts

1M HNO<sub>3</sub> = 1 parts

Q. 13 Draw the structure of rubenic acid





# Model Question Paper

Examination: B. A / B. Sc First Annual 2010

Subject: CHEMISTRY (Practical)

Time Allowed: 4 Hours

NOTE:

A: For Question No. 1

Record your experiments, observations & inferences systematically stepwise in tabular form and write the chemical equations wherever it is necessary and required. Show at least one confirmatory test of each radical to the examiner and get it signed for acknowledgement of performance.

B: For Question No. 2

- Write down balanced chemical equation, procedure and calculations based on supposed readings within first 15 minutes.
- A candidate must show a set of initial and final readings to the practical examiner and get them signed
- In case of gravimetric analysis, dry precipitate should be shown to the examiner.

- Q. 1 Analyze the given mixture 'M' by dry and wet tests systematically and determine two acid and two basic radicals present in the mixture.
- Q. 2 Determine the percentage purity of  $K_2Cr_2O_7$ . Given sample solution contains 8 g of impure  $K_2Cr_2O_7$  dissolved in 250 mL. 0.1M  $Na_2S_2O_3 \cdot 5H_2O$  solution is provided.
- Q. 3 Note Book & Viva Voce.

## Marking Scheme

### Q. 1 Mixture Analysis

- |  |            |
|--|------------|
| 1. Correct group detection of acid radicals  | 1          |
| 2. Identification of acid radicals           | 1          |
| 3. Confirmatory test (one for each radical)  | 2          |
| 4. Correct group detection of basic radicals | 1          |
| 5. Identification of basic radicals          | 1          |
| 6. Confirmatory test (one for each radical)  | 2          |
| <b>Total</b>                                 | <b>= 8</b> |

Presentation and write up should be systematic in tabular form.

### Q. 2 Volumetric Analysis

- |   |               |
|---|---------------|
| 1. Correct balanced Chemical Equation.                        | $\frac{1}{2}$ |
| 2. Indicator  | $\frac{1}{2}$ |
| 3. Procedure  | 1             |
| 4. Calculations from supposed readings.                       | 1             |
| 5. Calculations from actual observations with correct formula | 3             |
| <b>Total</b>  | <b>= 6</b>    |

Note: Deduct  $\frac{1}{3}$  mark for every 2% error in result.

### Gravimetric Analysis

- |   |                |
|---|----------------|
| 1. Balanced Chemical equation                         | $\frac{1}{2}$  |
| 2. Procedure & calculation from supposed observations | $1\frac{1}{2}$ |
| 3. Preparation of required solutions                  | $\frac{1}{2}$  |
| 4. Digestion, drying and weighing of ppt.             | $1\frac{1}{2}$ |
| 5. Result up to yield with (5%) error                 | 2              |
| <b>Total</b>  | <b>= 6</b>     |

### Paper Chromatography

- |                 |            |
|-----------------|------------|
| 1. Procedure.   | 1          |
| 2. Performance  | 1          |
| 3. Chromatogram | 2          |
| 4. $R_f$ values | 2          |
| <b>Total</b>    | <b>= 6</b> |

Note: Marking Scheme may differ slightly in different Universities.



Table of atomic weights of the elements

Names of Elements	Symbols	Approximate Atomic Mass	International Atomic Mass	Names of Elements	Symbols	Approximate Atomic Mass	International Atomic Mass
Actinium	Ac	227	227	Manganese	Mn	55	54.93
Aluminum	Al	27	26.981	Mercury	Hg	200.5	200.59
Antimony	Sb	122	121.75	Molybdenum	Mo	96	95.94
Argon	Ar	40	39.948	Neon	Ne	20	20.179
Arsenic	As	75	74.921	Nickel	Ni	59	58.693
Barium	Ba	137	137.33	Nitrogen	N	14	14.006
Beryllium	Be	9	9.012	Oxygen	O	16	15.999
Bismuth	Bi	209	208.98	Palladium	Pd	107	106.42
Boron	B	11	10.81	Phosphorus	P	31	30.97
Bromine	Br	80	79.90	Platinum	Pt	195	195.08
Cadmium	Cd	112.5	112.41	Potassium	K	39	39.098
Calcium	Ca	40	40.08	Radium	Ra	226	226.05
Carbon	C	12	12.01	Rubidium	Rb	85.5	85.47
Cerium	Ce	140	140.12	Samarium	Sm	150	150.36
Chlorine	Cl	35.5	35.45	Scandium	Sc	45	44.95
Chromium	Cr	52	51.99	Selenium	Se	79	78.96
Cobalt	Co	59	58.93	Silicon	Si	28	28.08
Copper	Cu	63.5	63.54	Silver	Ag	108	107.86
Fluorine	F	19	18.99	Sodium	Na	23	22.989
Gallium	Ga	70	69.72	Strontium	Sr	87.5	87.62
Germanium	Ge	72.6	72.61	Sulphur	S	32	32.06
Gold	Au	197	196.96	Tantalum	Ta	181	180.94
Helium	He	4	4.0026	Tellurium	Te	127.5	127.60
Hydrogen	H	1	1.0079	Terbium	Tb	159	158.92
Indium	In	115	114.82	Thorium	Th	232	232.03
Iodine	I	127	126.9	Tin	Sn	118.5	118.69
Iridium	Ir	192	192.2	Titanium	Ti	48	47.88
Iron	Fe	56	55.84	Tungsten	W	184	183.85
Krypton	Kr	84	83.80	Uranium	U	238	238.03
Lanthanum	La	139	138.905	Vanadium	V	51	50.94
Lead	Pb	207	207.2	Xenon	Xe	131	131.29
Lithium	Li	7	6.9341	Yttrium	Y	89	88.90
Lutetium	Lu	175	174.97	Zinc	Zn	65	65.39
Magnesium	Mg	24	24.31	Zirconium	Zr	91	91.22